Studies on Organometallic Aspects of Metalloporphyrin Chemistry Relevant to Heme Enzymatic Functions

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(Degree)
博士 (理学)
(Date of Degree)
1994-03-31
(Date of Publication)
2008-03-25
(Resource Type)
doctoral thesis
(Report Number)
甲1312
(JaLCDOI)
https://doi.org/10.11501/3078440
(URL)
https://hdl.handle.net/20.500.14094/D1001312

博士論文

Studies on Organometallic Aspects of Metalloporphyrin Chemistry Relevant to Heme Enzymatic Functions

（ヘム酵素機能に関連した有機金属ポルフィリンの化学に関する研究）

平成　六年　三月

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Studies on Organometallic Aspects of Metalloporphyrin Chemistry Relevant to Heme Enzymatic Functions

Yoshihiro Ishimaru

1994

Preface

The studies presented in this thesis have been carried out under the direction of Professor Akira Sera at the Department of Chemistry, Faculty of Science, Kobe University, during 1990-1994.

The author wishes to express his warmest gratitude to Professor Akira Sera. His kind guidance and continuous encouragement are deeply appreciated. The author also wishes to express his sincere thanks to Assistant Professor Jun-ichiro Setsune of Kobe university for his pertinent guidance and valuable discussion during the course of this work.

The author greatly indebted to Dr. Masaaki Sato of University of Osaka Prefecture, and Assistant Professor Hiroaki Ohoya of Kyoto university for the measurements of ESR spectra, and wishes to express their thanks for their valuable discussion.

The author is also sincerely grateful to Assistant Professor Hiroaki Yamada and Dr. Kuniaki Itoh of Kobe university and the late Professor Teijiro Kitao, Assistant Professor Masaru Matuoka, Dr. Hiroyuki Nakazumi and Dr. Masahiko Inouye of University of Osaka Prefecture, their helpful discussions and comments.

The other express her gratitude to the operator of instruments, Miss Masuko. Nishinaka, for the elemental analyses and mass spectra measurement.

Finally, the author wishes to thank his colleagues and my friends for their great kindness and friendly goodwill throughout the work.

Yoshihiro Ishimaru

March 1994

Contents

Chapter I

Chapter II

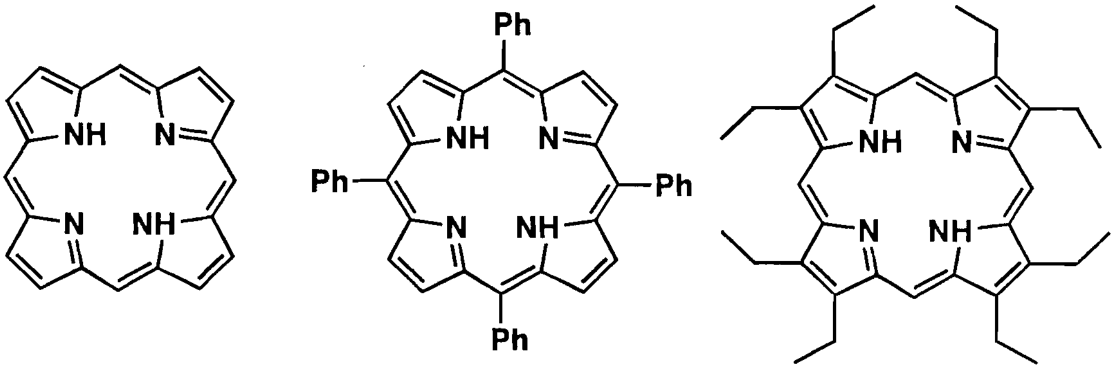
Chapter III

Chapter IV

Introduction

Massive contributions to our knowledge of the structure and function of heme proteins has been accumulated in the field of biochemistry.[1] Many biochemists have been studying on structures and functions of heme proteins themselves. Their structures and functions have been gradually revealed to be elegant and efficient. On the other hand, many chemists has been doing research on functions of heme proteins by using *mimic* of themselves.[2] For example, the model system of hemoglobin was investigated by J. H. Wang whose system attracted a great deal of attention as the first stable hemoglobin model and by J. P. Collman whose system suggested that one of the most important factors needed for oxygen carriers was to protect dimerization of iron porphyrins. Since these early works, various model systems of heme enzymes and heme proteins were constructed.

Porphyrins are formally constructed from porphin, which consists of four pyrrole rings jointed, by four methine bridges by substitution of the peripheral positions with various functional groups. The porphin macrocycle has 26 π-electrons, but only 18 of these are included in any delocalization pathway.[3] This conforms with Hückel's 4n+2 rule for aromaticity. There are two general useful porphin macrocycles. An octaethylporphyrin with eight ethyl groups is essential for its high symmetry that simplifies spectroscopic identification of the reaction products. Also, *meso*-tetraarylporphyrins with four aryl groups are most popular with easy synthetic methods so called Rothemund[4] synthesis. These porphyrin derivatives can be easily metallated and then are able to take various oxidation states. Metalloporphyrin derivatives with various metal ions in the center core and various substituent groups at the peripheral positions were used for model studies on photosynthesis,[5] hydoroxylation[6] and suicidal inactivation of cytochrome P-450,[7] vitamin B_{12} dependent reaction[8] and hemoglobin.[9] Especially, iron porphyrin derivatives were utilized for interesting the reactivities and properties of the hemoprotein model complexes. In this thesis I described fundamental aspects of metalloporphyin chemistry relevant to heme enzymatic functions.



Porphin *meso*-Tetraphenylporphyrin Octaethylporphyrin

Scheme 1. Structure of Representative Porphyrins

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Chapter I

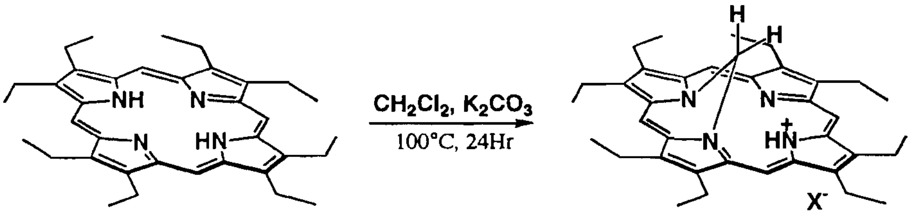
Formation of N^{21},N^{22}-Etheno Bridged *meso*-Tetraphenylporphyrin Hydroperchlorates; Simulation of Suicidal Inactivation of Cytochrome P-450.

Summary

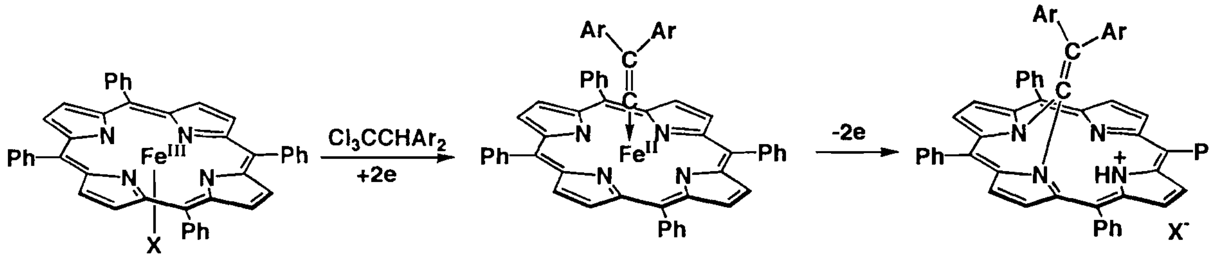
The formation of various N^{21},N^{22}-etheno-bridged *meso*-tetraphenylporphyrin hydroperchlorates was achieved in good yields by the oxidation of cobalt(II) porphyrin with ferric chloride or ferric perchlorate in the presence of various alkynes. In this chapter, syntheses, characteristics and reaction behaviors of these compounds are described.

Introduction

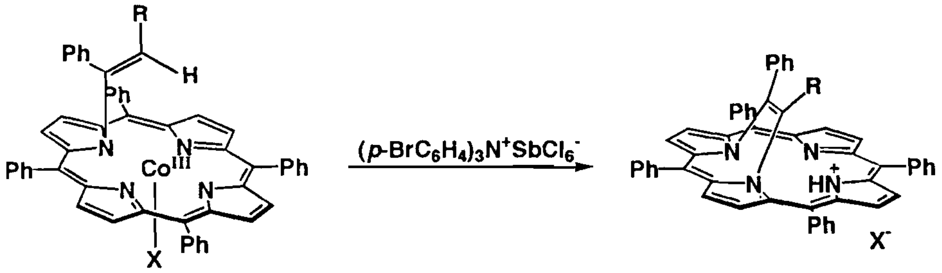
N^{21},N^{22}-Etheno bridged porphyrins[1] have been the focus of recent studies on the suicidal inactivation of cytochrome P-450 by 1-aminobenzotriazole and related compounds which are well-known as benzyne precursors.[2] These N^{21},N^{22}-bridged porphyrins are generally difficult to obtain because of the low reactivity of porphyrin nitrogen and the strain imposed by such a N^{21},N^{22}-bridge.



A. W. Johnson
(1975)



D. Mansuy
(1981)

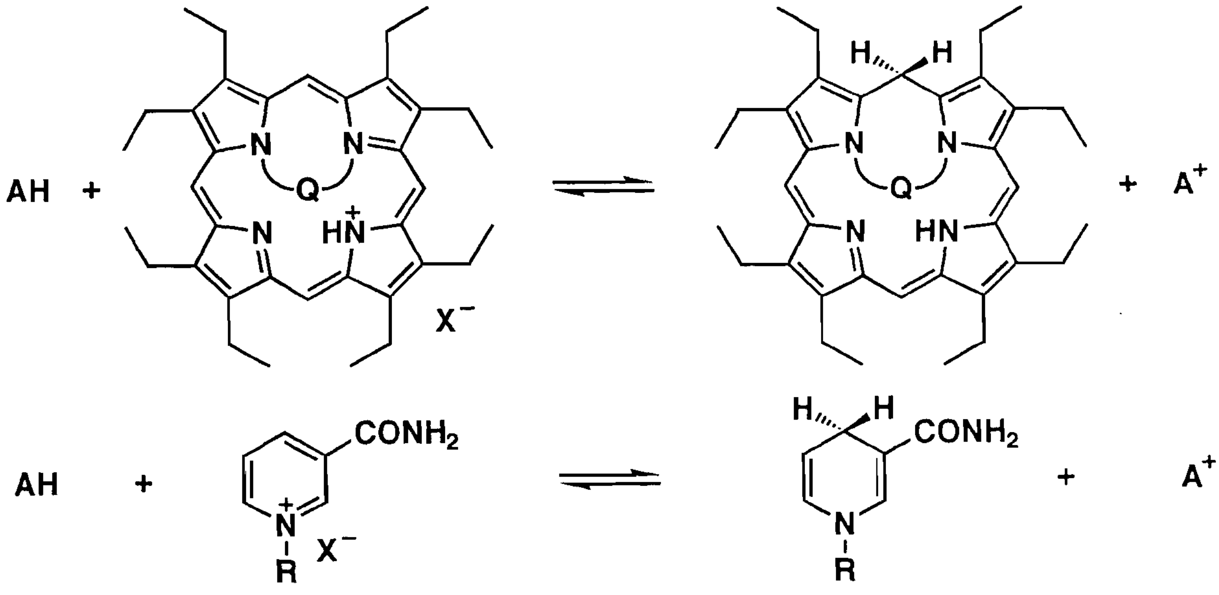


R = Me, Ph

H. J. Callot
(1985)

There are three synthetic methods; i) the reaction of free base porphyrins with organic polyhalides under basic conditions, which was reported by A. W. Johnson,[3] ii) the reaction of iron(II) porphyrins with DDT followed by oxidative rearrangement, which was reported by D. Mansuy,[4] iii) the reaction of *N*-aryl- or *N*-styrylporphyrins with $(p\text{-}BrC_6H_4)_3N^{\bullet +}SbCl_6^-$, which was reported by H. J. Callot.[5] Each method is restricted to only a few examples with relatively low yields. An elegant one-pot synthetic method of N^{21},N^{22}-bridged octaethylporphyrins via *Co*,*N*-etheno bridged intermediates was recently found in our laboratory.[6] Thus, I developed the synthesis of N^{21}, N^{22}-bridged analogues of other porphyrin macrocycles in this chapter.

The development of redox active heterocycles analogous to NAD^+ was achieved by the introduction of N^{21},N^{22}-etheno bridge.[7] These N^{21},N^{22}-etheno bridged porphyrins show marvelous properties arising from the extraordinarily strained molecular structure and the high basicity. The hydride anion attacked on the *meso* carbon regio- and stereoselectively. The above reaction afforded a phlorin form in which a sp^2 *meso*-carbon of a porphyrin nucleus was reduced to a sp^3 carbon bridge. In general, phlorins are unstable compounds under aerobic conditions.[8] But the resulting phlorin was stable enough to be treated under air. Therefore I started further investigations on the porphyrin-phlorin redox reaction.



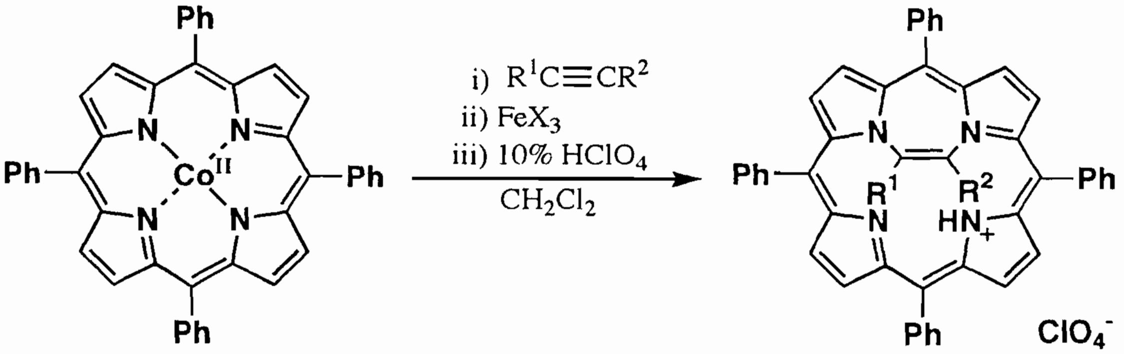
Scheme 1-2. Redox-active Heterocycles Analogous to NAD^+

The recent studies on metalloporphyrin π-cation radicals demonstrated that there are two types of Co^{III} porphyrin π-cation radicals[9] in the case of cobalt octaethylporphyrin (OEP). $[(OEP)^{+\bullet}Co(III)]Br_2$ (**1**) and $[(OEP)^{+\bullet}Co(III)](ClO_4)_2$ (**2**) have been regarded as representative of $^2A_{1u}$ and $^2A_{2u}$ states, respectively, on the basis of optical and ESR evidence, and the similarity of their optical absorption spectra to those of catalase compound I (CAT-I) and horseradish peroxidase compound I (HRP-I) was noted.[10] It has recently been shown that **2** prepared by the oxidation of divalent octaethylporphyrin with ferric perchlorate reacts smoothly with alkynes to give *N*^{21},*N*^{22}-etheno bridged octaethylporphyrin hydroperchlorates[6] whereas **1** does not react at all. The reason why **1** does not react with various acetylenes is that the reaction of metalloporphyrins with various acetylenes requires the contribution of a vacant metal orbital in the axial direction. As far as **1** is concerned, two Br^- ions occupies axial sites on the porphyrin complexes. But **2** possesses two ClO_4^- as counter anions. Since the redox potentials and the electronic states in the Co(III) complexes of octaethylporphyrin π-cation radical are considerably different from these of tetraarylporphyrin π-cation radical, it is of interested to study on the reactivity of the latter toward acetylenes. Then I investigated the reaction of $[TPPCo(III)](X)_2$ ($X=FeCl_4^-$, ClO_4^-) with alkynes.

Results and Discussion

Synthesis and Spectroscopic Properties of *N*^{21},*N*^{22}-Etheno Bridged *meso*-Tetraphenylporphyrin Hydroperchlorates

Cobalt(II) *meso*-tetraphenylporphyrin reacted with alkynes, such as diphenyl acetylene, 2-butyne-1,4-diol, phenyl acetylene, propargyl alcohol, 1-hexyne, acetylene, in the presence of oxidizing agent, such as $FeCl_3$ or $Fe(ClO_4)_3$, under aerobic atmosphere in CH_2Cl_2 solution to cause the color change from red to green. The mixture was dealt with 10% $HClO_4$ aqueous solution, and then purification by chromatography on silica gel eluted with CH_2Cl_2-acetone (10:1) afforded N^{21},N^{22}-etheno-bridged *meso*-tetraphenylporphyrin hydroperchlorates (**3**-**8**) in moderate to good yields. $FeCl_3$ is preferred for monosubstituted acetylene, while $Fe(ClO_4)_3$ is preferred for disubstituted acetylene as shown in Table 1-1.



Scheme 1-3. Synthesis of N^{21},N^{22}-Etheno Bridged $TPPHClO_4$

Compd.	**3**	**4**	**5**	**6**	**7**	**8**
R^1	Ph	CH_2OH	Ph	CH_2OH	C_4H_9	H
R^2	Ph	CH_2OH	H	H	H	H

Table 1-1. The Yields of **3**–**8** by The Use of $FeCl_3$ and $Fe(ClO_4)_3$

Oxidant	**3**	**4**	**5**	**6**	**7**	**8**
$FeCl_3$	44	–	45	67	47	47
$Fe(ClO_4)_3$	90	75	–	–	–	–

A considerable amount of a by-product was isolated in the case of acetylene gas through oxidizing by $FeCl_3$. That is, introduction of acetylene gas into a mixture of $(TPP)Co^{II}$ and $FeCl_3$ in CH_2Cl_2 at room temperature gave **8** as a main product(47%) and *N*-(β-chlorovinyl)*meso*-tetraphenylporphyrinatocobalt(II) thiocyanide (**9**) as a by-product(33%) after the treatment with sat. NaSCN aqueous solution and then purification by chromatography on silica gel. The best procedure to obtain **8** (66%) exclusively is the treatment of $(TPP)Co^{II}$ with acetylene gas in CH_2Cl_2 at 0 °C for one hour followed by the addition of $FeCl_3$ (5 fold molar excess) in the absence of oxygen. As far as acetylene was concerned, $FeCl_3$ was preferred to $Fe(ClO_4)_3$. The compound **9** could be easily demetallated by the treatment with trifluoroacetic acid for about 15 minute and the neutralization of the resulting solution with aqueous ammonia gave *N*-(β-chlorovinyl)-*meso*-tetraphenylporphyrin free base (**10**).

Table 1–2. The ^{1}H–NMR Spectral Data and The Yields of **9–10** (in $CDCl_3$)

Compd.	β–Pyrrole	*o*–	*m*–	*p*–	Vinyl	Yield
9	44.2, 35.9 1.6, −1.9	23.3, 19.6 2.5, −3.0	13.5, 12.2 7.3, 7.1	9.5 7.6	−69.6 −95.1	33
10	8.91, 8.99 8.46, 8.61		7.6–8.4		−1.45 2.30	90

The compound **9** shows paramagnetic ^{1}H-NMR spectrum with a C_s symmetric pattern which is characteristic of N-substitution. The free base **10** derived from **9** was unambiguously characterized as *N*-(β-chlorovinyl)(TPP)H on the basis of the spectral data of *N*-vinyl(TPP)H which have been reported by H. J. Callot[5c]. Ordinarily, extensive use was made of the deuterated and methylated analogous as well as comparisons of line widths and intensities to determine the assignments in the paramagnetic NMR spectra. But a detailed comparison of paramagnetic ^{1}H-NMR and 2D-cosy spectra of **9**, shown in Figure 1-1 and 1-2, allowed us to assign β-pyrrole protons, and *o*-, *m*-, and *p*- protons of *meso*-aryl substituents. Signals at 23.3, 12.2, 9.5, 7.1, and 2.5 ppm due to the one set of aryl substituents were correlated by the appearance of the major cross peaks, while signals at 19.6, 13.5, 7.6, 7.3, and -3.0 ppm due to another set of aryl substituents were correlated by another set of major cross peaks. Therefore, signals at 44.2, 35.9, 1.6, and -1.9 ppm are associated to β-pyrrole protons, 23.3, 19.6, 2.5, and -3.0 ppm to *o*-phenyl protons, 13.5, 12.2, 7.3, and 7.1 ppm to *m*-phenyl protons, 9.5, and 7.6 ppm to *p*-phenyl protons, and -69.6 and -95.1 ppm to vinylene protons for **9**. The estimate of dipolar and contact shifts compared with other *N*-vinyl complexes will be discussed in chapter

III. The *trans*-β-chlorovinyl structure of **9** was suggested by the coupling constant of the vinyl signals of **10** (12.2 Hz) due to *trans* configuration.

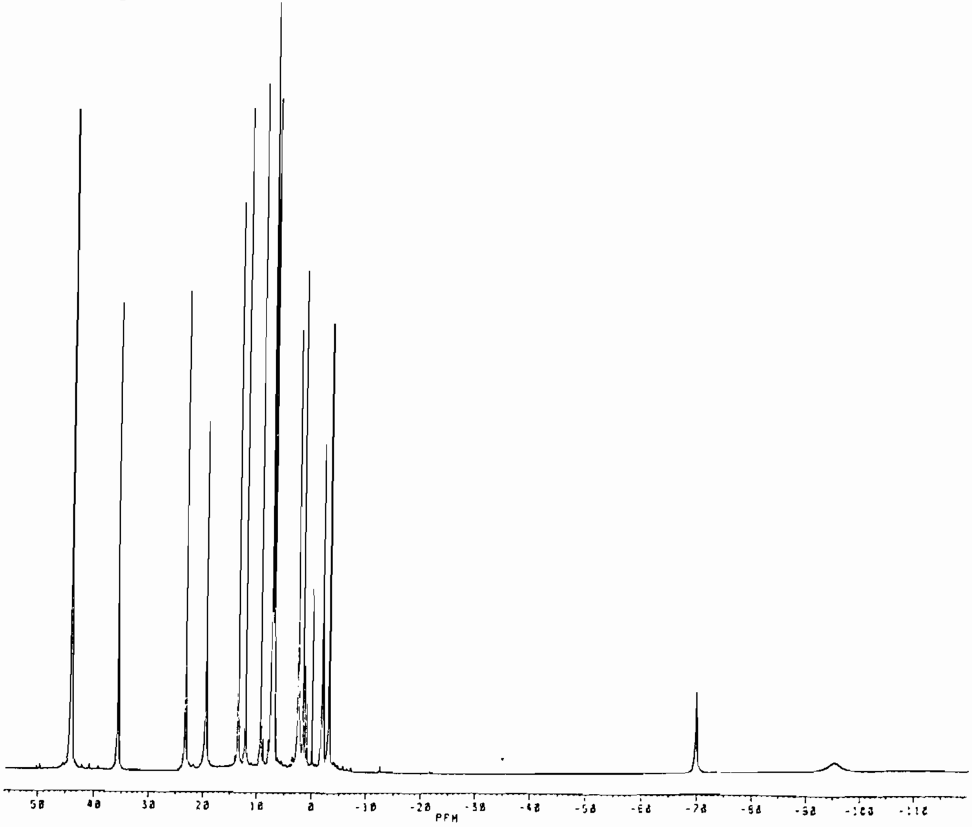


Figure 1-1. ^{1}H-NMR Spectra of Complex **9**

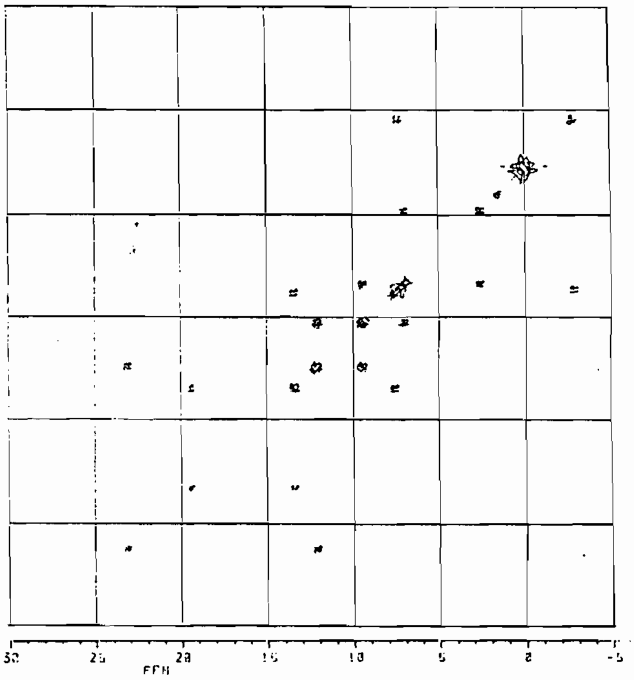


Figure 1-2. 2D-COSY Spectra of Complex **9**

Table 1-3. λ_{max} Values of N^{21},N^{22}-Etheno Bridged *meso*-Tetraphenylporphyrin Hydroperchlorates **3-8** (in CH_2Cl_2)

Compd.	λ_{max} Value (log ε)			
3	432(5.15),	557(3.93),	593(4.10),	641(3.73)
4	429(5.09),	554(3.89),	590(4.02),	640(3.73)
5	430(5.08),	561(3.88),	596(4.04),	648(3.83)
6	429(5.02),	557(3.85),	593(3.99),	647(3.79)
7	429(5.07),	559(3.87),	594(4.04),	646(3.79)
8	431(5.00),	560(3.97),	600(3.99),	644(3.81)

Table 1-4. λ_{max} Values of *N*-(CH=HCl)TPPCo(II)SCN and *N*-(CH=HCl)TPPH$^+$ (in CH_2Cl_2)

Compd.	λ_{max} Value (log ε)				
9	447(5.10),	569(3.92),	618(4.05),	667(3.80)	
10	433(5.14),	529(3.84),	569(4.00),	617(3.82),	672(3.60)

The compound **3-8** possess quite similar UV-Vis spectra (see Table 1-3) typical of N-substitution which makes a Soret band to shift to a longer wavelength (about 430 nm) and a Q-band to take a three-banded shape (so called Rhodo type). Although **9** shows a similar UV-Vis spectrum to those of **3-8**, the absorption maxima are red-shifted by 10-20 nm in comparison with those of **3-8**. Furthermore, **10** shows a four-banded visible absorption characteristic of a free base chromophore (see Figure 1-3).

The ^{1}H-NMR spectral data of **3-8** are summarized in Table 1-5. The ^{1}H-NMR spectra show four doublets with equal intensity due to the β-pyrrole protons for **3**, **4**, and **8** which were synthesized from symmetrical alkynes. These porphyrins possess C_s symmetry. In the case of **5**, **6**, and **7** which were synthesized from unsymmetrical alkynes the ^{1}H-NMR spectra show eight doublets with equal intensity due to the β-pyrrole protons. These compounds show the upfield shifted peaks due to the bridge substituents as expected from the theory that the region over a porphyrin plane is magnetically anisotropic due to the porphyrin ring current effect.

Table 1-5. The ^{1}H-NMR Spectral Data of **3**-**8** (in $CDCl_3$)

Compd.	β-Pyrrole	Others
3	8.77(d,2H), 8.92(d,2H) 9.19(d,2H), 9.15(d,2H)	2.65(b,1H,*o*-Ph), 5.95(b,2H,*m*-Ph) 6.34(dd,2H,*p*-Ph), -2.7(b,1H,NH)
4	8.79(d,2H), 8.92(d,2H) 9.02(d,2H), 9.05(d,2H)	-2.29, 0.28(dd,2Hx2,$C\underline{H}_2OH$) 1.35(dd,1Hx2,$CH_2O\underline{H}$) -2.7(b,1H,NH)
5	8.56(d,2H), 8.84(d,2H) 8.87(d,2H), 8.91(d,2H) 9.02(d,2H), 9.03(d,2H) 9.22(d,2H), 9.23(d,2H)	-1.48(s,1H,Vinyl-H) 2.33(d,2H,*o*-Ph), 5.83(t,2H,*m*-Ph) 6.21(t,1H,*p*-Ph), -3.1(b,1H,NH)
6	8.71(d,2H), 8.84(d,2H) 8.90(d,2H), 8.96(d,2H) 9.00(d,2H), 9.02(d,2H) 9.04(d,2H), 9.05(d,2H)	-1.08(s,1H,Vinyl-H) -1.71, -1.28(dd,1Hx2,$C\underline{H}_2OH$) 0.66(dd,1Hx2,$CH_2O\underline{H}$) -3.3(b,1H,NH)
7	8.74(d,2H),8.86(d,2H) 8.87(d,2H),8.97(d,2H) 8.99(d,2H),9.00(d,2H) 9.02(d,2H),9.05(d,2H)	-1.38(s,1H,Vinyl-H) -3.69,-2.99(q,1Hx2,$C\underline{H}_2C_3H_7$) -1.29,1.72(dq,1Hx2,$CH_2C\underline{H}_2C_2H_5$) -0.58(m,2H,$C_2HC_4\underline{H}_2CH_3$) -0.10(t,3H,$C_3H_6C\underline{H}_3$)
8	8.78(d,2H),8.93(d,2H) 8.95(d,2H),8.99(d,2H)	-1.08(s,1H,Vinyl-H)

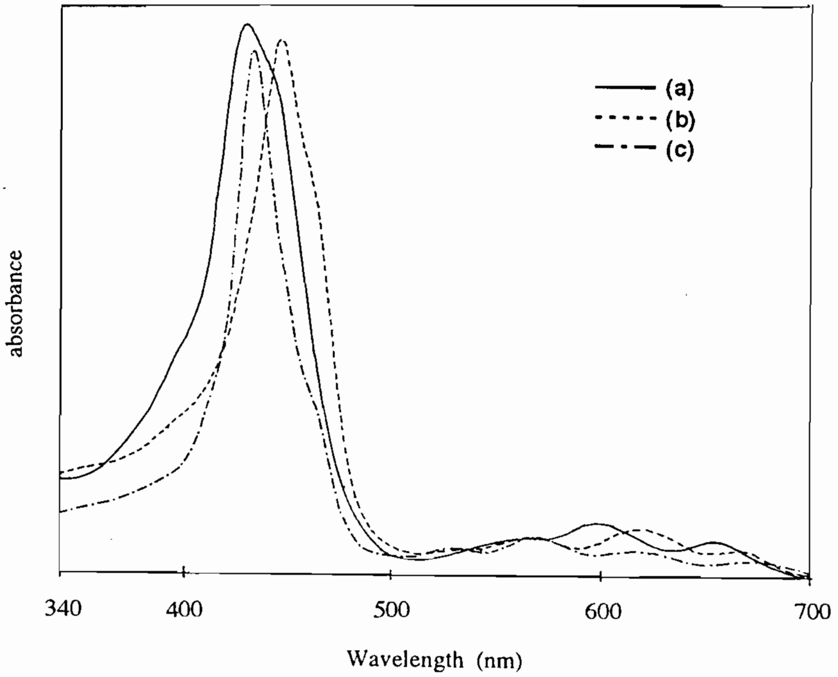


Figure 1-3. UV-Vis Spectra in CH_2Cl_2 of (a) **8**, (b) **9** and (b) **10**

The singlet near -1.5 ppm is associated with the bridge vinylene proton which is observed at around -2.5 ppm in the case of a N^{21},N^{22}-etheno bridged octaethylporphyrin hydroperchlorates.[6] One factor attributed to this difference in the chemical shifts is the electron density of the conjugated π-system which are influenced by the peripheral substituents[11]. The ortho and meta protons of the bridge aryl groups of **3** appear as two broad signals at 2.65 ppm and 5.93 ppm at 25 °C in contrast to the sharp signals at 2.33 ppm and 5.83 ppm due to the ortho and meta protons of bridge aryl group of **5** (see Figure 1-4). This is indicative of the restricted rotation of the two phenyl groups of in the *cis*-stilbene type structure **3** at 25 °C.

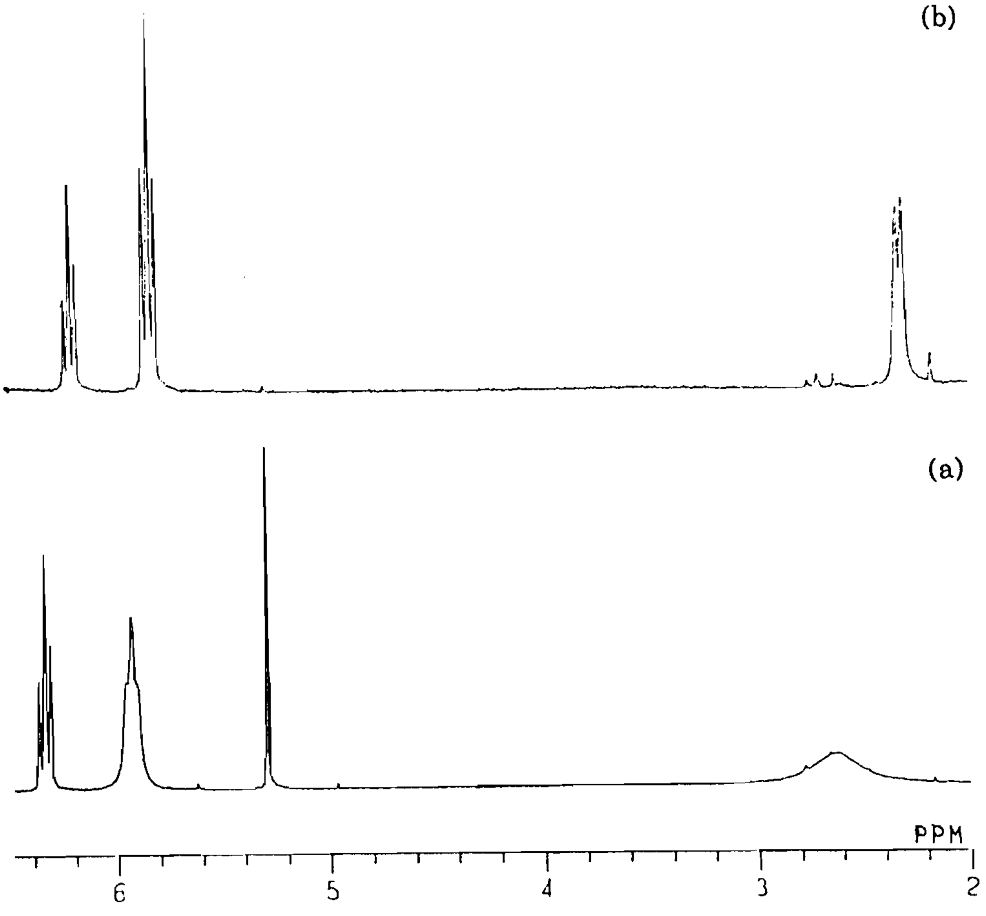
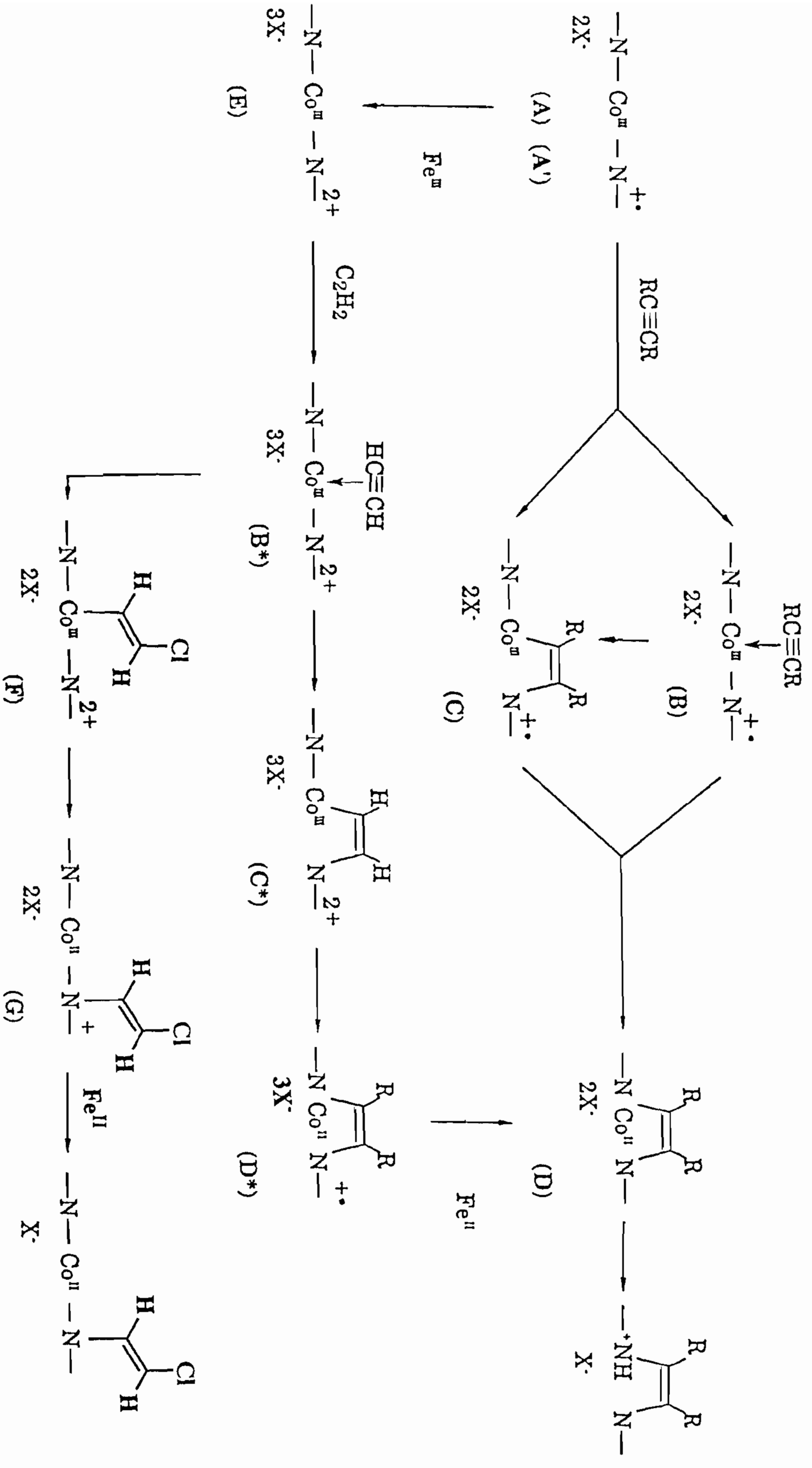


Figure 1-4. ^{1}H-NMR Spectra of Aromatic Region of (a) **3**, (b) **9**

The IR spectra of **3-8** showed intense absorptions due to ClO_4^- ion which was derived from the treatment with 10% $HClO_4$ in the work-up procedure. Since it has been well-known that the introduction of *N*-substituted groups accelerates demetallation, metal complexes of **3**-**8** could not be detected.

A proposed reaction mechanism is shown in Scheme 1-4. A previous study using OEP ligand has shown that the Co^{III} π-cation radicals (**A**) prepared from divalent cobalt porphyrin with $FeCl_3$ or $Fe(ClO_4)_3$ play a key role by forming the organometallic intermediates such as an acetylene π-complex of Co^{III} π-cation radical (**B**) and a *Co,N*-etheno bridged Co^{III} π-cation radical (**C**). These intermediates can be rearranged into N^{21},N^{22}-etheno bridged Co^{II} porphyrin (**D**) and then converted into the corresponding monocations. Although Co^{III}(OEP) π-cation radical (**A**) was quite stable in the presence of excess $Fe(ClO_4)_3$, monitoring UV-Vis spectral change during the oxidation of $(TPP)Co^{II}$ with excess $Fe(ClO_4)_3$ clearly showed that the initially generated Co^{III}(TPP) π-cation radical (**A'**) is further oxidized to Co^{III}(TPP) π-dication (**E**) in agreement with the results obtained from the electrochemical oxidation of $(TPP)Co^{II}$.[13] Therefore, π-dication (**E**) is formed when a mixture of $(TPP)Co^{II}$ and Fe^{III} salt is allowed to react well prior to the addition of alkynes. As long as disubstituted alkynes are used,π-dication **E** gave N^{21},N^{22}-etheno-bridged porphyrins in a similar yield to that from the π-cation radical **A**. However, the reaction of acetylene gas afford *N*-(β-chlorovinyl)porphyrin **9** under the conditions where π-dication **E** is formed. This phenomenon is rationalized in terms of the competition between porphyrin nitrogen and chloride when Co^{III} acetylene π-complex intermediates (**B** and **B***) undergo nucleophilic attack on the acetylene ligand to lead to a *Co,N*-etheno bridged complex (**C** and **C***) and a σ-(β-chlorovinyl)Co^{III} complex (**F**), respectively. Since the porphyrin nitrogen of Co^{III}(TPP) π-dication should be less reactive than that of the π-cation radical, nucleophilic attack of chloride takes place in the case of π-dication to give **F** which spontaneously undergoes Co-to-N migration of the organo ligand to give *N*-(β-chlorovinyl)$(TPP)Co^{II}$ π-cation radical (**G**). According to this mechanism, substituents on the acetylene should make greater steric hindrance toward intermolecular attack of chloride than intramolecular attack of porphyrin nitrogen. Thus,

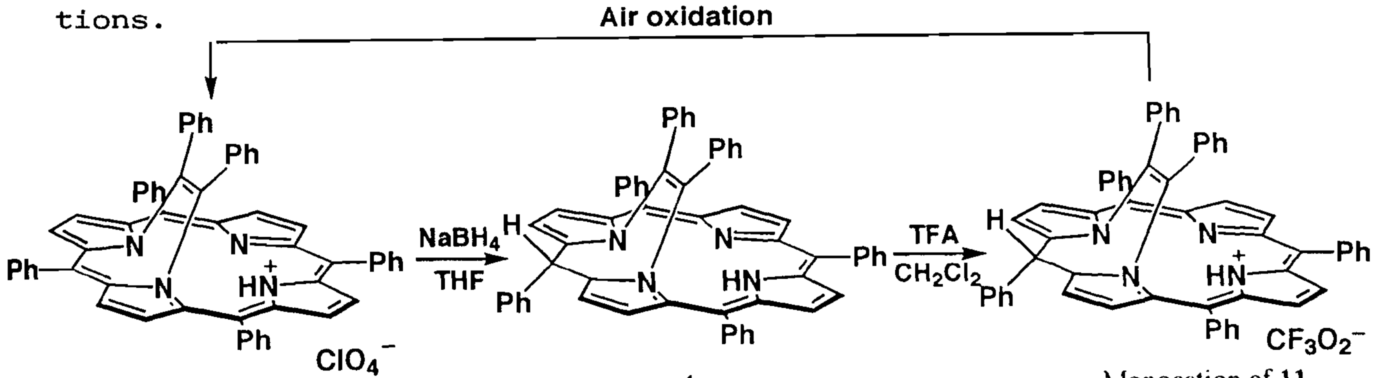


Scheme 1-4. Reaction Mechanism

the reaction of the π-dication **E** with disubstituted alkynes seems to proceed by way of **C*** which is rearranged to N^{21},N^{22}-etheno bridged Co^{II} porphyrin π-cation radical (**D***).

Porphyrin-Phlorin Redox Chemistry of N^{21},N^{22}-Etheno-Bridged Porphyrin Hydroperchlorates

N^{21},N^{22}-Etheno-bridged porphyrins are expected to show novel properties based on the molecular strain and high basicity induced by the N^{21},N^{22}-bridged structure. Indeed, it has been reported that N^{21},N^{22}-etheno-bridged octaethylporphyrin hydroperchlorates are reduced regioselectively and stereoselectively at the 5-*meso*-carbon to give the 5*H*-phlorin[7] which shows a visible band at about 640 nm. Treatment of **3** with $NaBH_4$ (3 fold molar excess) in THF gave a green blue compound which could be extracted into n-hexane. Removal of n-hexane afforded satisfactorily pure powders of N^{21},N^{22}-(1,2-diphenyletheno)*meso*-tetraphenyl-5*H*-phlorin (**11**) in 39% yield. While N^{21},N^{22}-(1,2-diphenyletheno)octaethyl-5*H*-phlorin was so rapidly air-oxidized to the corresponding porphyrin under acidic conditions that the phlorin monocation could not be obtained as a stable compound, treatment of **11** with a slightly excess amount of trifluoroacetic acid[7] in CH_2Cl_2 resulted in the quantitative formation of its monocation which was air-oxidized slowly in ten hours under these conditions.



3

4

Monocation of 11

Scheme 1-5. Porphyrin-Phlorin Redox

Figure 1-4 shows the UV-Vis spectra of **11** and its monocation which are characteristic of a phlorin chromophore but with an extremely red-shifted visible band up to 800 nm. Mass spectrum of **11** showed an intense peak at 793(M^++1) corresponding to the calculated mass for $C_{58}H_{40}N_4$.

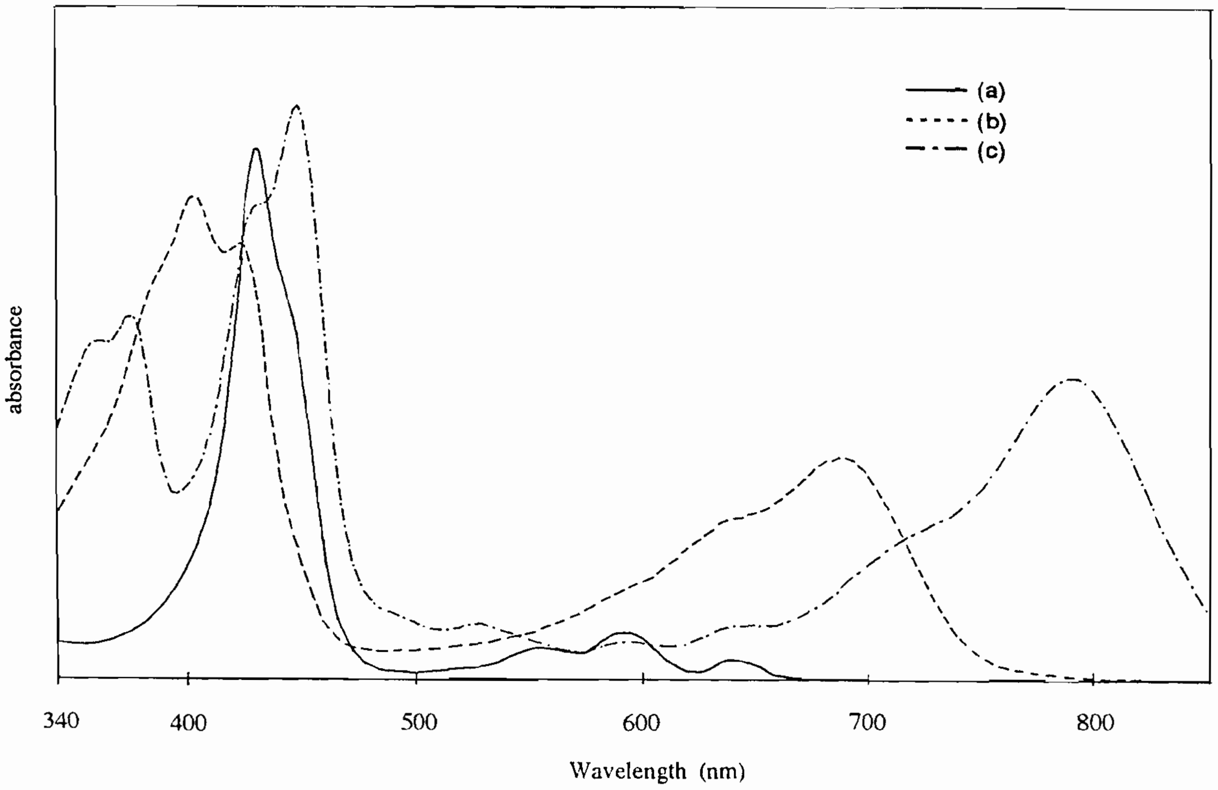


Figure 1-5. UV-Vis Spectra in CH_2Cl_2 of (a) **3**, (b) **11** and Monocation of **11**

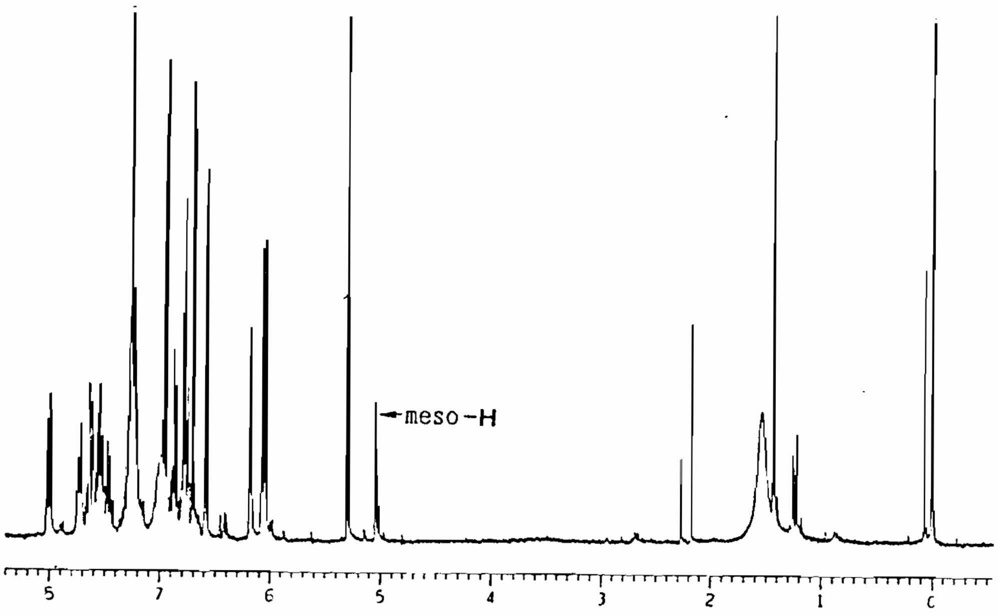
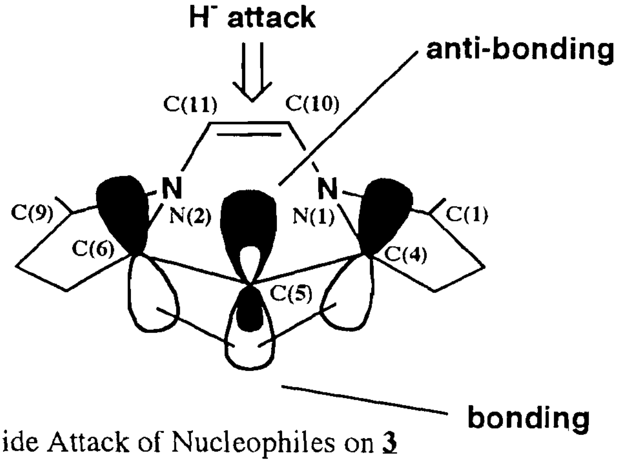


Figure 1-6. ^{1}H-NMR Spectra of **11**

The ^{1}H-NMR spectrum of **11** revealed that a ring current effect based on porphyrin π-electrons disappeared according to the formation of 5*H*-phlorin. Four doublets due to the β-pyrrole protons appeared with equal intensity in an ordinary pyrrole proton region at 6.17, 6.58, 6.70, and 6.95 ppm, and also two double doublets and one triplet (2:2:1 ratio) due to the bridge aryl protons appeared at 6.05, 6.77, and 6.87 ppm, respectively. A singlet due to the saturated *meso* methine proton appeared at 5.04 ppm in the ^{1}H-NMR spectra of **11** while signals due to the 5-*exo* and the 5-*endo* proton of the corresponding octaethyl-5*H*-phlorin are observed at 3.53 and 5.36 ppm, respectively[7]. As a phenyl substituent generally causes a 1-2 ppm downfield shift in the ^{1}H-NMR, the 5-*meso* methine proton of **11** is considered to take an *exo*-side. This is consistent with the fact that the addition of deuteride occurred from the *exo* side of the 5-*meso* carbon of N^{21},N^{22}-(1,2-diphenyletheno)(OEP)$HClO_4$.

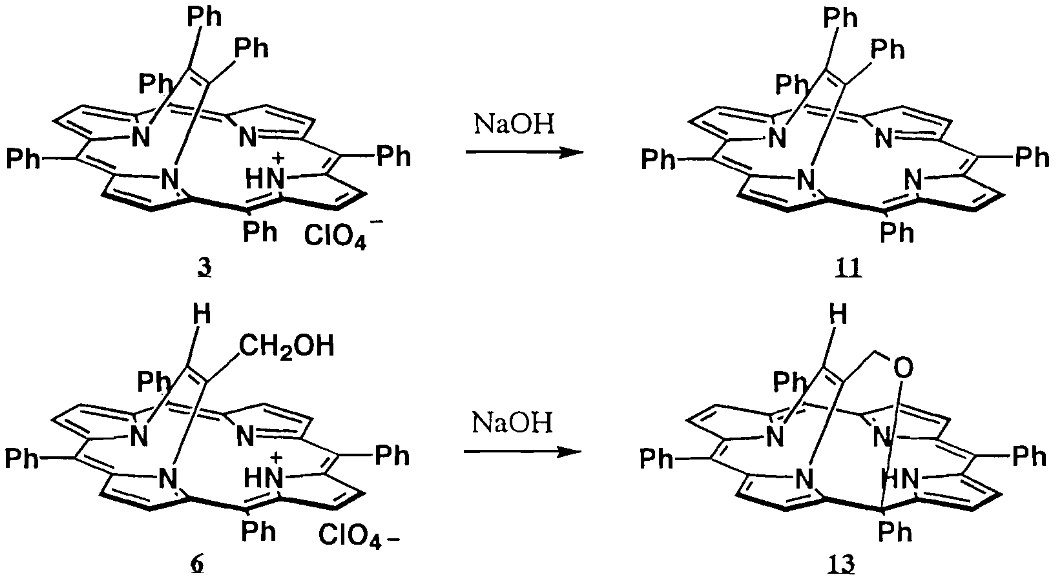
Selected Bond Angles (deg.)

C(10)-N(1)-C(1)	123.9
C(10)-N(1)-C(4)	118.1
C(11)-N(2)-C(6)	118.1
C(11)-N(2)-C(9)	122.0



Scheme 1-6. *Exo*-Side Attack of Nucleophiles on **3** under the Stereoelectronic Control.

The introduction of a N^{21},N^{22}-etheno bridging group exerts a strain on a porphyrin plane so that the 5-*meso* carbon favors a tetrahedral configuration. According to the X-ray structural analysis[5c] on **3**, pyrrole rings are tilted with respect to the porphyrin plane so that a greater overlap of the p-orbital of the 5-*meso* carbon is expected to occur with that of C(4) or C(6) in the *endo* region than in the *exo* region. Therefore the anti-bonding π-orbital which interacts with a nucleophile should extend more to the *exo* side at the 5-*meso* carbon to account for the exclusive *exo*-side attack of nucleophiles. This rationalizes the observed stereoselectivity, and a similar stereoelectronic effect should be expected for the NAD$^+$ model compound which are closely related to **3-8** in the sense that they are monocationic nitrogen heterocycles. These phlorins and their monocations which can be dissolved in hexane, absorb at 690 and 791nm, and are stable against air oxidation would be used as near infrared absorbing dyes.



Scheme1-6. Porphyrin-Phlorin Redox

Addition of 10% NaOH aqueous solution (ca. 10 ml) to CH_2Cl_2 solution could afford its free base (**12**) showing the color change from green to brown-green, immediately. The yield was 53%. When **6** was treated with 10% NaOH aqueous solution of **11** in the same manner, a novel 10*H*-phlorin (**13**) was formed in 60% yield with showing the color change from green to blue. The UV-Vis spectrum of **12** shows a four-banded visible absorption characteristic of a free base chromophore and **13** was unambiguously characterized as a phlorin on the basis of the broad visible band with maximum intensity at 672 nm. Mass spectrum of **13** showed an intense peak at 669(M$^+$+1) corresponding to the calculated mass for $C_{47}H_{32}N_4O$.

Figure 1-8 shows ^{1}H-NMR spectrum of **6** and **13**. The bridge o-methylene protons (H_A and H_B) which appear as two doublet of doublets at -1.71 and -1.28 ppm (J_{gem}=14.0 Hz and J_{vic}=4.0, 9.2

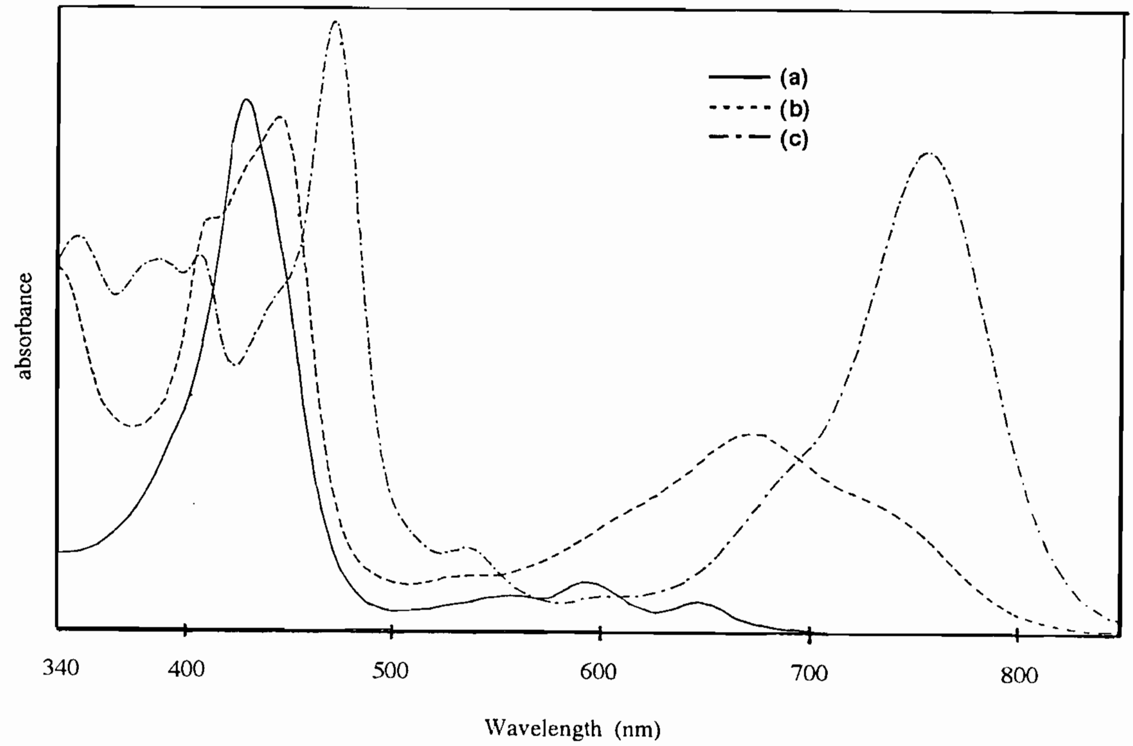


Figure 1-7. UV-Vis Spectra in CH_2Cl_2 of (a) **6**, (b) **13** and (c) Monocation of **13**

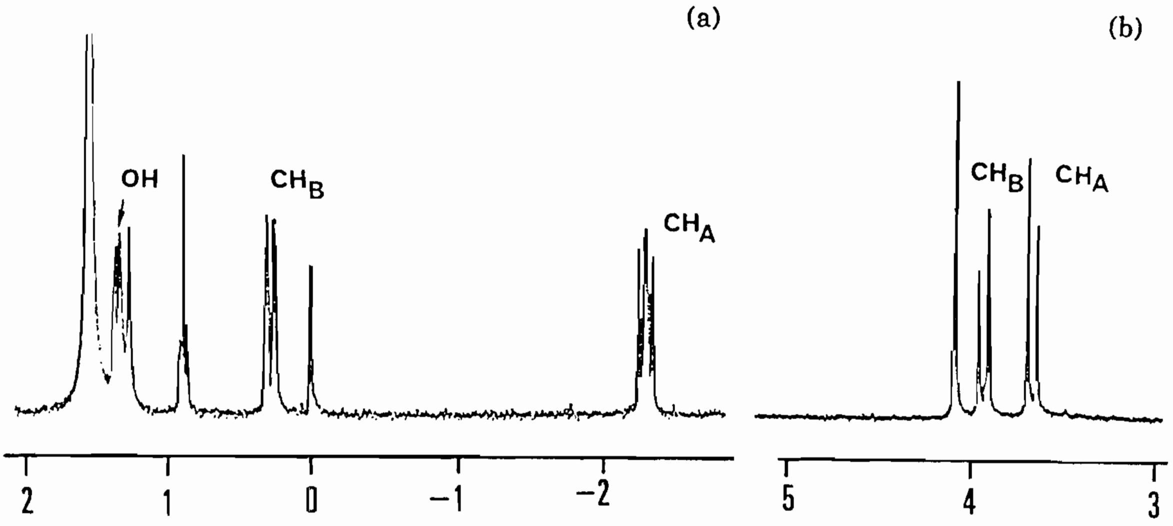


Figure 1-8. ^{1}H-NMR Spectra of Bridged Groups of (a) **6** and (b) **13**

Table 1-6. λ_{max} Values of **11**-**13** and Their Salts (in CH_2Cl_2)

Compd.	λ_{max} Value (log ε)				
11	405(4.63),	426(4.51),	690(4.30)		
11$^{a)}$	361(4.48),	346(4.51),	450(4.71),	791(4.44)	
12	441(5.01),	544(4.02),	585(3.81),	628(3.75),	677(3.55)
13	446(4.56),	672(4.15)			
13$^{a)}$	349(4.45),	389(4.42),	408(4.42),	472(463),	756(4.52)

a) In the presence of trifluoro acetic acid

Hz) for **6** were observed as two doublets (J_{gem}=13.5 Hz) at 3.68 and 3.96 ppm for **13**. This spectral change is best explained by the nucleophilic attack of the bridge alkoxide anion not on the 5-*meso* carbon but on the 10-*meso* carbon of **6**, because the bridge hydroxymethyl group comes closer to the 10-*meso* position than the 5-*meso* position as judged from a molecular model.

Table 1-7. The ^{1}H-NMR Spectral Data **11-13** (in $CDCl_3$)

Compd.	β-Pyrrole	Others	Yield
11	6.17(d,2H), 6.58(d,2H) 6.70(d,2H), 6.95(d,2H)	6.60(dd,1H,*o*-Ph), 6.77(t,2H,*m*-Ph) 6.87(d,2H,*p*-Ph), 5.04(s,1H,*meso*-H)	39
12	8.21(d,2H), 8.47(d,2H) 8.61(d,2H), 8.63(d,2H)	3.0(b,1H,*o*-Ph), 5.80(b,2H,*m*-Ph) 6.15(b,2H,*p*-Ph)	53
13	6.43(d,2H), 6.48(d,2H) 6.49(d,2H), 6.81(d,2H) 6.85(d,2H), 6.96(d,2H) 7.08(d,2H), 7.10(d,2H)	4.09(s,1H,Vinyl-H) 3.68, 3.96(dd,1Hx2,CH_2O)	60

Table 1-8. The List of Elemental Analysis Data

Compd.	Formula		H	C	N
3	$C_{58}H_{39}N_4ClO_4$	Found	4.04	72.58	6.16
		(Calc.)	(4.41)	(78.15)	(6.29)
4	$C_{48}H_{35}N_4ClO_6$	Found	4.22	70.57	6.88
		(Calc.)	(4.41)	(72.13)	(7.01)
5	$C_{52}H_{35}N_4ClO_4$	Found	4.27	76.78	6.55
		(Calc.)	(4.33)	(76.60)	(6.87)
6	$C_{47}H_{33}N_4ClO_5$	Found	4.24	70.56	7.07
		(Calc.)	(4.32)	(73.38)	(7.29)
7	$C_{50}H_{39}N_4ClO_4$	Found	4.79	74.14	7.15
		(Calc.)	(4.94)	(75.51)	(7.04)
8	$C_{46}H_{31}N_4ClO_4$	Found	4.15	72.58	7.61
		(Calc.)	(4.23)	(74.74)	(7.58)
9	$C_{47}H_{30}N_5SClCo$	Found	3.86	73.23	9.15
		(Calc.)	(3.82)	(71.35)	(8.85)
10	$C_{46}H_{31}N_4Cl$	Found	4.18	73.95	6.91
		(Calc.)	(4.62)	(81.82)	(8.30)
11	$C_{58}H_{40}N_4$	Found	4.42	85.39	7.35
		(Calc.)	(5.08)	(87.85)	(7.07)
12	$C_{58}H_{38}N_4$	Found	4.67	85.39	7.08
		(Calc.)	(4.84)	(88.07)	(7.08)
13	$C_{47}H_{32}N_4O$	Found	4.56	81.96	8.22
		(Calc.)	(4.82)	(84.41)	(8.38)

Experimental Sections

General Comments. ^{1}H-NMR spectra were recorded in deuteriochloroform by using a JEOL GX-270 spectrometer (270 MHz), and chemical shifts are referenced to tetramethylsilane. Coupling constants of pyrrolic and aromatic protons are in a normal range about 5 and 8Hz, respectively, and will not be specified. UV-Vis spectra were taken in dichloromethane solution on a Shimadzu UV-240 or a Shimadzu-UV-245Fs spectrometer. IR spectra measurements were made in a KBr disk with a Shimadzu IR-420 spectrometer. Elemental Analyses were performed on a Yanaco CHN MT2 recorder using acetanilide as a standard compound. Wakogel C-300 was used for silica gel column chromatography. Most reactions were monitored by using a Kieselgel 60F254 silica gel TLC plate. *Meso*-tetraphenylporphyrin free base and *meso*-tetraphenylporphyrinatocobalt(II) was prepared by literature procedure[9].

Formation of N^{21},N^{22}-Etheno Bridged *meso*-Tetraphenylporphyrin Hydroperchlorates

General Procedure ; TPPCo(II) (ca. 100 mg) was completely dissolved in CH_2Cl_2 (ca. 120 ml). An alkyne (ca. 3eq) and an oxidizing agent such as $FeCl_3$ or $Fe(ClO_4)_3$ (5 fold molar excess) were added to the solution. The color of reaction mixture changed from red to green within half an hour. When the color does not change, the oxidizing agent (2 fold molar excess) was further added to the solution. This reaction mixture was stirred for about one hour at ambient temperature under aerobic atmosphere. After the reaction completed, the reaction mixture was dealt with 10% $HClO_4$ aqueous solution (ca. 30 ml) in a separatory funnel. The CH_2Cl_2 layer was successively washed with water twice, and then dried over Na_2SO_4. After removal of CH_2Cl_2, the residue was chromatographed on silica gel with CH_2Cl_2-acetone (10:1) to purify the desired product which could be collected as a green band with a red color fluorescence. Recrystallization from CH_2Cl_2-hexane afforded N^{21},N^{22}-etheno(TPP)$HClO_4$ (**3-8**).

N^{21},N^{22}-(PhC=CPh)TPPHClO$_4$ 3 ; The reaction was performed by using $FeCl_3$ in the presence of diphenyl acetylene. According to the general procedure, compound 3 was obtained in 44% yield. On the other hand, using $Fe(ClO_4)_3$ in the presence of diphenyl acetylene gave **3** in 90% yield according to the general procedure: ^{1}H-NMR δ($CDCl_3$) 8.77, 8.92, 9.12, 9.15 (doubletx4, 2Hx4, β-pyrrole), 2.65 (broad, 4H, bridge o-Ph), 5.93 (broad, 4H, bridge *m*-Ph), 6.34 (doublet of doublets, 2H, bridge *p*-Ph), 7.0~8.6 (multiplet, 20H, *meso*-Ph), -2.7 (broad, 1H, NH); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 432(5.15), 557(3.93), 593(4.10), 641(3.73); Anal. Calcd for $C_{58}H_{39}N_4O_4Cl$: C,78.15; H,4.41; N,6.29. Found. C,72.58; H,4.04; N,6.16.

N^{21},N^{22}-(HOCH$_2$C=CCH$_2$OH)TPPHClO$_4$ 4 ; The reaction was performed by using $Fe(ClO_4)_3$ in the presence of 2-butyne-1,4-diol. According to the general procedure, compound **4** was obtained in 75% yield. On the other hand, using $FeCl_3$ in the presence of 2-butyne-1,4-diol gave no products according to the general procedure: ^{1}H-NMR δ($CDCl_3$) 8.79, 8.92, 9.02, 9.05 (doubletx4, 2Hx4, β-pyrrole), -2.29, 0.28 (doublet of doublets, 2Hx2, bridge CH_2OH, J_{gem}=15.0, J_{vic}=3.4, 11.3 Hz), 1.35 (doublet of doublets, 1Hx2, bridge CH_2OH, J_{vic}=11.1, 3.4 Hz), 7.8~8.7(multiplets, 20H, *meso*-Ph) -3.1 (broad, 1H, NH); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 429(5.09), 554(3.89), 590(4.02), 540(3.73); Anal. Calcd for $C_{48}H_{35}N_4O_6Cl$: C,72.13; H,4.41; N,7.01. Found. C,70.57; H,4.22; N,6.88.

N^{21},N^{22}-(HC=CPh)TPPHClO$_4$ 5; The reaction was performed by using $FeCl_3$ in the presence of phenyl acetylene. According to the general procedure, compound **5** was obtained in 45% yield. On the other hand, using $Fe(ClO_4)_3$ in the presence of phenyl acetylene gave no product according to the general procedure: ^{1}H-NMR δ($CDCl_3$) 8.56, 8.84, 8.87, 8.91, 9.02, 9.03, 9.22, 9.24 (singletx8, 1Hx8, β-pyrrole), -1.48 (singlet, 1H, vinyl-H), 2.33 (doublet, 2H, bridge *o*-Ph), 5.83 (triplet, 2H, bridge *m*-Ph), 6.21 (triplet, 1H, bridge *p*-Ph), -3.1 (broad, 1H, NH), 7.8~8.3 (multiplet, *meso*-Ph); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 430(5.08), 561(3.88), 596(4.04), 6.48(3.83); Anal. Calcd for $C_{52}H_{35}N_4O_4Cl$: C,76.60; H,4.33; N,6.87. Found. C,76.78; H,4.27; N,6.55.

N^{21},N^{22}-(HC=CCH$_2$OH)TPPHClO$_4$ 6 ; The reaction was performed by using $FeCl_3$ in the presence of propargyl alcohol. According to the general procedure, compound **6** was obtained in 67% yield. On the other hand, using $Fe(ClO_4)_3$ in the presence of propargyl alcohol gave no products according to the general procedure: ^{1}H-NMR δ($CDCl_3$) 8.71, 8.84, 8.90, 8.96, 9.00, 9.02, 9.04, 9.05 (doubletx8, 1Hx8, β-pyrrole), -1.08 (singlet, 1H, bridge vinyl-H), -1.71, -1.28 (doublet of doubletsx2, 1Hx2, bridge-CH_2OH, J_{gem}=14.0 Hz, J_{vic}=4.0, 9.2 Hz), 0.66 (doublet of doublets, 1H, bridge -CH_2OH, J_{vic}=4.6, 9.5 Hz), 7.7~8.6 (multiplets, 20H, *meso*-Ph), -3.3 (broad, 1H, NH); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 429(5.02), 557(3.85), 595(3.99), 647(3.78); Anal. Calcd for $C_{47}H_{33}N_4O_5Cl$: C,73.38; H,4.32; N,7.28. Found. C,70.56; H,4.24; N,7.07.

N^{21},N^{22}-(HC=CC$_4$H$_9$)TPPHClO$_4$ 7 ; The reaction was performed by using $FeCl_3$ in the presence of 1-hexyne. According to the general procedure, compound was obtained in 47% yield: ^{1}H-NMR δ($CDCl_3$) 8.74, 8.86, 8.87, 8.97, 8.99, 9.00, 9.02, 9.05 (doubletx8, 2Hx8, β-pyrrole), -1.38 (singlet, 1H, bridge vinyl-H), -3.69, -2.99 (quintet, 1Hx2, bridge -$CH_2C_3H_7$), -1.29, -1.72 (doublet of quartetx2, 1Hx2, bridge -$CH_2CH_2C_2H_5$), -0.58 (multiplet, 2H, bridge -$C_2H_4CH_2CH_3$), -0.10 (triplet, 3H, bridge -$C_3H_6CH_3$), 7.4~8.8 (multiplet, 20H, *meso*-Ph); UV-Vis(CH_2Cl_2) λ_{max}(log ε) 429(5.07), 559(3.87), 594(4.04), 646(3.79); Anal. Calcd for $C_{50}H_{39}N_4O_4Cl$: C,75.51; H,4.94; N,7.04. Found. C,74.14; H,4.79; N,7.15.

N^{21},N^{22}-(HC=CH)TPPHClO$_4$ 8 (Method A); The reaction was performed by using $FeCl_3$ in the presence of acetylene. According to the general procedure, compound **8** and *N*-(HC=CHCl)TPPCo^{II}SCN which was obtained after the treatment with saturated NaSCN aqueous solution were obtained in 47% and 33% yields, respectively: ^{1}H-NMR δ($CDCl_3$) 8.78, 8.93, 8.95, 8.99 (doubletx4, 2Hx4, β-pyrrole), -1.69 (singletsx2, 1Hx2, bridge vinyl-H), 7.8~8.3 (multiplets, 20H, *meso*-Ph); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 431(5.00), 560(3.97), 600(3.99), 654(3.81); Anal. Calcd for $C_{46}H_{31}N_4O_4Cl$: C,74.74; H,4.23; N,7.58. Found. C,72.58; H,4.15; N,7.61.

***N*-(CH=CHCl)TPPCo(II)SCN 9**; See above reaction procedure. Recrystallization of **9** was performed from CH_2Cl_2-methanol: ^{1}H-NMR δ($CDCl_3$) 44.2, 35.9, 1.6, -1.9 (singletx4, 2Hx4, β-pyrrole), 23.3, 19.6, 2.5, -3.0 (singletx4, 2Hx4, *meso-o*-Ph), 13.5, 12.2, 7.3, 7.1 (singletx4, 2Hx4, *meso-m*-Ph), 9.5, 7.6 (singletx4, 2Hx4, *meso-p*-Ph), -69.6, -95.1 (singletx2, 1Hx2, vinyl-H); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 447(5.10), 569(3.94), 618(4.05), 667(3.80); Anal. Calcd for $C_{47}H_{30}N_5SClCo$: C,71.35; H,3.82; N,8.85. Found. C,73.23; H,3.86; N,9.15

***N*-(CH=CHCl)TPPH 10** ; Trifluoroacetic acid (ca. 1ml) was added to **9** dissolved in CH_2Cl_2. After stirring for 15 minutes, the reaction mixture was neutralized with aqueous ammonia. The CH_2Cl_2 layer was separated, washed with water, dried over Na_2SO_4, and evaporated. The residue was recrystallized with CH_2Cl_2-hexane to give *N*-(β-chlorovinyl)-*meso*-tetraphenylporphyrin free base (**10**) in 90% yield: ^{1}H-NMR δ($CDCl_3$) 8.91, 8.99, 8.46, 8.61 (singletx2, doubletx2, 2Hx4, β-pyrrole), -1.45, 2.30 (doubletx2, 1Hx2, bridge vinyl-H J_{trans}=12.2 Hz) 7.6~8.4 (multiplet, 20H, *meso*-Ph); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 433(5.14), 529(3.84), 569(4.00), 617(3.82), 672(3.60); Anal. Calcd for $C_{46}H_{31}N_4Cl$: C,81.82; H,4.63; N,8.30. Found. C,73.95; H,4.18; N,6.91

N^{21},N^{22}-(HC=CH)TPPHClO$_4$ 8 (Method B); TPPCo(II) (ca. 100 mg) was placed in a four necked flask fitted with a sealed rubber septum, a gas inlet port for introducing acetylene gas, a swan necked glass cell containing $FeCl_3$ (5 fold molar excess), and a three-way stop-cock which was joined to a vacuum pump and a balloon. When the atmosphere was replaced with acetylene gas, CH_2Cl_2 (ca. 150 ml) was added with syringe via a sealed rubber septum.

Acetylene gas was allowed to bubble for half an hour at 0 °C, before an oxidizing agent was added into this solution. The color of the reaction mixture changed from red to green when $FeCl_3$ was added. After stirring for an hour at 0 °C, the reaction mixture was dealt with 10% $HClO_4$ aqueous solution (ca. 30 ml) in a separatory funnel. The CH_2Cl_2 layer was successively washed with water twice, and dried over Na_2SO_4. After removal of CH_2Cl_2, the residue was chromatographed on silica gel with CH_2Cl_2-acetone (10:1) in order to purify the desired product which could be collected as a first green band. The second green band was identified as compound **10**. Recrystallization from CH_2Cl_2-hexane gave **8** in 66% yield.

Formation of N^{21},N^{22}-(1,2-Diphenyletheno)*meso*-Tetraphenyl-5*H*-Phlorin 11

$NaBH_4$ (3 fold molar excess) was added to N^{21},N^{22}-(1,2-diphenyletheno)*meso*-tetraphenylporphyrin perchlorate **3** (50 mg) in THF. The color of the reaction mixture changed from green to blue. After stirring for half an hour, THF was evaporated. The residue was dissolved in n-hexane. The filtered n-hexane solution was evaporated and the residue recrystallized from CH_2Cl_2-methanol to give N^{21},N^{22}-(1,2-diphenyletheno)*meso*-tetraphenyl-5*H*-phlorin **11** in 39% yield: ^{1}H-NMR δ($CDCl_3$) 6.17, 6.58, 6.70, 6.95 (doublet of doublets, doubletx3, 2Hx4, β-pyrrole), 6.06 (doublet of doublets, 4H, bridge *o*-Ph), 6.77 (triplet, 4H, bridge *m*-Ph), 6.87 (doublet, 2H, bridge *p*-Ph), 5.04 (singlet 1H, *meso*-H), 6.8~8.5 (multiplet, 20H, *meso*-Ph); MS m/e 793(M^++1); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 405(4.63), 426(4.51), 690(4.30); Anal. Calcd for $C_{58}H_{40}N_4$: C,87.85; H,5.08; N,7.07. Found. C,85.39; H,4.42; N,7.35.

Monocation ; UV-Vis(CH_2Cl_2) λ_{max} (log ε) 361(4.48), 346(4.51), 450(4.71), 791(4.44)

Formation of N^{21},N^{22}-(1,2-Diphenyletheno)*meso*-Tetraphenylporphyrin Free Base 12

The CH_2Cl_2 solution of N^{21},N^{22}-(1,2-diphenyletheno)*meso*-tetraphenylporphyrin perchlorate **3** (50 mg) was treated with 10% NaOH aqueous solution under aerobic atmosphere at room temperature. The color of the reaction mixture changed immediately from green to brown-green. After stirring the reaction mixture for half an hour, a CH_2Cl_2 layer was separated and dried over Na_2SO_4. The residue which was given by removal of CH_2Cl_2 was dissolved in ether. The filtered ether solution was evaporated to afford N^{21},N^{22}-(1,2-diphenyletheno)*meso*-tetraphenylporphyrin free base **12** in 40% yield: ^{1}H-NMR δ($CDCl_3$) 8.21, 8.47, 8.61, 8.63 (doubletx4, 2Hx4, β-pyrrole), 6.8~8.5 (multiplet, 2H, *meso*-Ph), -3 (broad, 4H, bridge *o*-Ph), 5.80 (broad, 4H, bridge *m*-Ph), 6.15 (broad, 2H, bridge *p*-Ph); MS m/e 793(M^++3); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 441(5.01), 544(4.02), 585(3.81), 628(3.75), 677(3.55); Anal. Calcd for $C_{58}H_{38}N_4$: C,88.07; H,4.84; N,7.08. Found. C,85.39; H,4.67; N,7.08.

Formation of N^{21},N^{22}-(1-Hydroxymethyletheno)*meso*-Tetraphenyl-10*H*-Phlorin 13

The CH_2Cl_2 solution of N^{21},N^{22}-(1-hydroxymethyletheno)*meso*-tetraphenylporphyrin hydroperchlorate **6** (50 mg) was treated with 10% NaOH aqueous solution under aerobic atmosphere at room temperature. The color of the reaction mixture changed immediately from green to blue. After stirring the reaction mixture for half an hour, a CH_2Cl_2 layer was separated and dried over Na_2SO_4. The residue which was given by removal of CH_2Cl_2 was dissolved in n-hexane. The n-hexane filtrate could afford N^{21},N^{22}-(1-hydroxymethyletheno)*meso*-tetraphenyl-10*H*-phlorin **13** in 60% yield: ^{1}H-NMR δ($CDCl_3$) 6.43, 6.48, 6.49, 6.81, 6.85, 6.96, 7.08, 7.10 (doubletx8, 1Hx8, β-pyrrole), 3.68, 3.96 (doubletx2, 1Hx2, bridge CH_2 J_{gem}=13.5Hz), 4.09 (singlet, 1H, bridge vinyl-H), 7.4~8.1 (multiplet, 20H, *meso*-Ph); Ms m/e 669(M^++1); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 446(4.56), 672(4.15); Anal. Calcd for $C_{47}H_{32}N_4O$: C,84.41; H,4.82; N,8.38. Found. C,81.96; H,4.56; N,8.22.

Monocation ; UV-Vis(CH_2Cl_2) λ_{max} (log ε) 349(4.45), 389(4.42), 408(4.42), 472(4.63), 756(4.52)

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Chapter II

Reactions of Cationic Cobalt(III) Porphyrin Perchlorates with Various Alkynes in The Presence of Bulky Amine; Simulation of the Interaction of Heme Proteins with Small Molecule by Using Organometallic Synthetic Analogous

Summary

Bis(aquo) *meso*-tetraphenylporphyrinatocobalt(III) perchlorate, (TPP)$Co^{III}(H_2O)_2ClO_4$ (**1a**), and bis(aquo)octaethylporphyrinatocobalt(III) perchlorate, (OEP)$Co^{III}(H_2O)_2ClO_4$ (**1b**), which give (por)Co^{II} π-cation radicals in non-polar solvents, reacted immediately with various alkynes in the presence of a bulky amine such as 2,6-lutidine to give novel σ-(β-2,6-lutidiniumvinyl)-cobalt(III) complexes (**2**-**7**) via $Co^{II}(por)^{+\bullet}$-alkyne π-complex intermediate. Furthermore, it was found that **1a** and **1b** reacted with acetylenes with electron-attracting substituents in the absence of a bulky amine to give novel *Co,N*-etheno bridged cobalt(III) porphyrins (**8**,**9**). These compounds play a key role in the formation of N^{21},N^{22}-etheno bridged porphyrins. Moreover, **1a** and **1b** reacted with an extra pure acetylene gas to give *N,N'*-vinylene bisporphyrins. ^{1}H-NMR, ESR, and UV-Vis spectral studies suggested that $Co^{II}(por)^{+\bullet}$ alkyne π-complex was in thermal equilibrium with *N,N'*-vinylene bisporphyrin biscobalt bisperchlorate.

Introduction

The field of organometalloporphyrin has been developed for past twenty years. The chemical behaviors of cationic cobalt(III) porphyrins have been reported by several groups[1]. Especially, their alkyne or alkene π-complexes[2] are of interest in modeling the possible intermediate for coenzyme B_{12}-dependent rearrangement as well as heme protein-dependent processes such as oxygen transportation, oxygen storage, and oxygen activation. But it is unusual for the metalloporphyrin alkyne or alkene π-complexes to be isolated and characterized. There are a few examples of these complexes. J. P. Collman reported that a diamagnetic Mo^{II} diphenyl acetylene π-complex[3] was given by the reduction of (TTP)$Mo^{IV}Cl_2$ (TTP : *meso*-tetra-*p*-tolylporphyrin dianion) by $LiAlH_4$ in the presence of diphenyl acetylene, and that a diamagnetic Os^{II} or Ru^{II} ethylene π-complex[4] ocurred in the reaction of the corresponding Os^0 or Ru^0 dianion with 1,2-

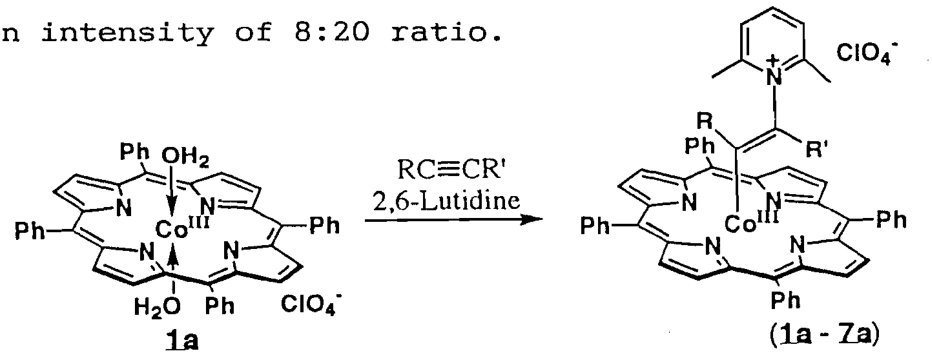
dichloroethane. The ^{1}H-NMR study of (β-hydroxyethyl)rhodium porphyrin complex recently suggested that Rh^{III} ethylene π-complex[5] could be generated in the presence of CF_3COOH or CF_3SO_3H at low temperature. Although investigation on the electronic structure of cationic cobalt(III) porphyrin perchlorates by optical absorption and resonance Raman spectra[6] suggested the existence of π-cation radical species in non-polar solvents, the chemical behavior of these cobalt(III) complexes has scarcely been known. It is intended in this chapter to provide insight into the reactions of cationic cobalt(III) porphyrin perchlorate with various alkynes to give novel σ-(β-2,6-lutidiniumvinyl)cobalt(III) porphyrins in the presence of a bulky amine such as 2,6-lutidine.[7] The reaction intermediate is discussed on the basis of the ^{1}H-NMR, ESR, and UV-Vis spectral measurements.

Results and Discussion

Reaction of Cationic Cobalt(III) Perchlorates in The Presence of a Bulky Amine

Addition of various alkynes to CH_2Cl_2 solution of (TPP)Co^{III}(H_2O)$_2$ClO$_4$ (**1a**) and (OEP)Co^{III}(H_2O)$_2$ClO$_4$ (**1b**) in the presence of a bulky amine such as 2,6-lutidine gave novel σ-(β-2,6-lutidiniumvinyl)Co^{III}(por)ClO$_4$ (**2-7**) in 9-58% yields and in 30-77% yields, respectively, after chromatography on silica gel with CH_2Cl_2-acetone (10:1). Preparation of **2a-7a** and **2b-4b** was summarized in Table 2-1. The UV-Vis spectra of (TPP)Co^{III}-R (**2a-7a**) and (OEP)Co^{III}-R (**2b-4b**) show sharp absorption bands characteristic of the σ-alkyl cobalt(III) porphyrins. Soret peaks were observed at 410 nm for **2a-7a** and 395 nm for **2b-4b** and Q-band peaks at 555 nm for **2a-7a** and 550 nm for **2b-4b**.

The *trans* addition of cobalt and 2,6-lutidine to acetylene was verified by the coupling constant (J_{trans}=13.1 Hz) between vinylic protons in the ^{1}H-NMR spectra of **7a**. In general, upfield chemical shifts of the σ-vinyl moiety in the ^{1}H-NMR spectra are explained in terms of the porphyrin ring current effect due to aromaticity of the conjugated π-system. The similarity of the ^{1}H-NMR chemical shifts of the 2,6-lutidine moiety of these complexes suggests the *trans* addition. That is, a doublet at 6.62 ppm due to β-lutidine protons and a triplet at 7.38 ppm due to a γ-lutidine proton observed for **2a** are in the chemical shift range very close to those of other σ-vinyl complexes (**3a**-**7a** and **2b**-**4b**). The TPP ligand of (**2a**-**7a**) has a C_{4v} symmetry and shows a singlet at about 10.5 ppm due to the β-pyrrole protons and multiplets between 7.5~8.5 ppm due to the *meso*-phenyl protons with the integration intensity of 8:20 ratio.



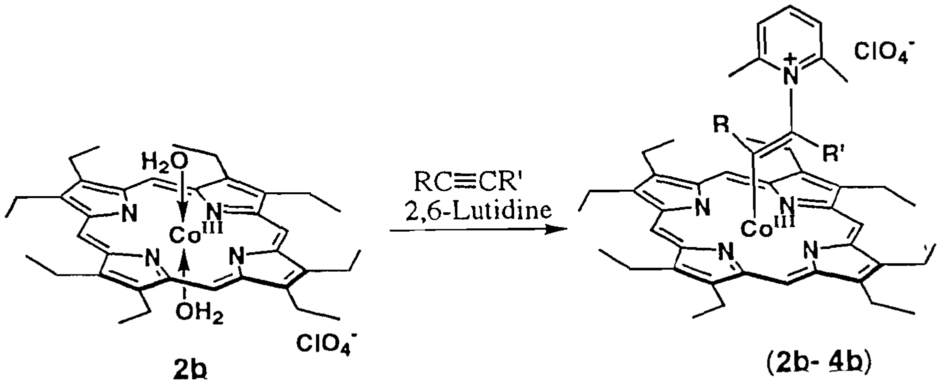


Table 2-1. Synthesis of σ-(β-2,6-Lutidiniumvinyl)Co^{III}(por)ClO_4

entry	1	R	R'	compd.	yield
1	1a	CO_2Me	H	2a	58
2	1a	H	Ph	3a	34
3	1a	H	CH_2OH	4a	9[a)]
	1a	CH_2OH	H	4a'	
4	1a	CO_2Me	Ph	5a	52
5	1a	CO_2Me	CO_2Me	6a	31
6	1a	H	H	7a	14
7	1b	CO_2Me	H	2b	77
8	1b	H	Ph	3b	49
9	1b	H	CH_2OH	4b	30[a)]
	1b	CH_2OH	H	4b'	

a) Total yield

Table 2-2. The ^{1}H-NMR Spectral Data of **2a**-**7a** (in $CDCl_3$)

Compd.	Porphyrin Ligand		Others			
	β-Py	Phenyl	α[a)]	β[a)]	R[b)]	2,6-Lutidine
2a	8.98	8.16,7.79	-	-0.21	1.70(s)	0.39(s), 6.62(d) 7.38(t)
3a	8.89	8.02,7.77	0.20	-	3.70(d), 6.73(t) 6.95(t)	0.49(s), 6.94(d) 7.72(t)
4a	8.95	8.10,7.77	-0.31	-	-1.80(d), 0.24(t)	0.49(s), 6.62(d) 7.32(t)
4a'	8.97	8.10,7.77	-	-1.42	-0.15(d), 1.64(t)	0.43(s), 6.62(d) 7.32(t)
5a	8.86	8.04,7.78	-	-	1.82(s), 4.08(d) 6.88(t), 7.13(t)	0.96(s), 6.90(d) 7.56(t)
6a	8.91	8.11,7.79	-	-	1.78(s), 2.42(s)	0.83(s), 7.17(d) 7.65(t)
7a	8.95	8.11,7.78	-0.06	0.56 (J=13.1)	-	0.27(s), 6.70(d) 7.40(t)

a) α and β denote Co–CH= and Co–C=CH– proton, respectively.
b) Protons due to substituents on the σ-vinyl group.

The OEP ligand of (**2b**-**4b**) similarly shows one singlet at about 10.0 ppm due to the *meso*-H, one doublet of quartets at about 4.0 ppm due to the methylene-H, and one triplet at about 1.9 ppm due to the methyl-H with the integration intensity of 1:4:6 ratio. The ^{1}H-NMR data of **2b** and **3b** indicate that the negatively polarized sp carbon of the original alkyne is attacked by cobalt and the positively polarized sp carbon is attacked by 2,6-lutidine. That is, the selective decoupling of the vinylic proton of **2b** at -1.22 ppm caused remarkable enhancement of the ^{13}C-signal due to the vinylic carbon at 115.8 ppm. Because a ^{13}C-NMR signal due to the Co-bound carbon is not observed due to

Table 2-3. The ^{1}H-NMR Spectral Data of **2b**-**4b'** (in $CDCl_3$)

Compd.	Porphyrin Ligand			Others			
	meso	CH_2	CH_3	$\alpha^{a)}$	$\beta^{a)}$	$R^{b)}$	2,6-Lutidine
2b	10.33(s)	4.08(dq)	1.88(t)	-	-1.22	1.44(s)	0.09(s), 6.54(d) 7.32(t)
3b	10.07(s)	3.99(dq)	1.84(t)	-0.51	-	3.40(d), 6.55(t) 6.86(t)	0.20(s), 6.77(d) 7.59(t)
4b	10.27(s)	4.07(dq)	1.87(t)	-0.89	-	-2.47(d), -1.03(t)	0.13(s), 6.51(d) 7.22(t)
4b'	10.15(s)	4.03(dq)	1.84(t)	-	-1.99	-0.68(d), 0.77(t)	0.16(s), 6.50(d) 7.22(t)

a) α and β denote Co-CH= and Co-C=CH- proton, respectively.
b) Protons due to substituents on the σ-vinyl group.

the quadrupolar relaxation effect of Co(I=7/2), the vinylic proton must not be bonded to the Co-bound carbon. This means that the nucleophilic attack of 2,6-lutidine takes place at the terminal carbon of methyl propiolate which is positively charged. A similar ^{1}H-^{13}C correlation NMR experiment for **3b** shows that the nucleophilic attack of 2,6-lutidine takes place at the internal sp carbon of phenyl acetylene which is also positively charged. The similarity of the chemical shifts of the carbomethoxy group and the phenyl group of **5a** to those of the corresponding group of **2a** and **3a** guarantees the structure in which the carbomethoxy group and the phenyl group are bound to the α-and β-position, respectively. On the other hand, the reaction of **1a** with propargyl alcohol afforded a mixture of two isomers in 1:1 ratio under the same reaction conditions. Thus, the directing effect of an alkyl substituent on an alkyne is not so overwhelming as phenyl and carbomethoxy substituents. The IR spectra of all these adducts showed two absorption bands due to ClO_4^- ion at 1100, 620 cm^{-1}.

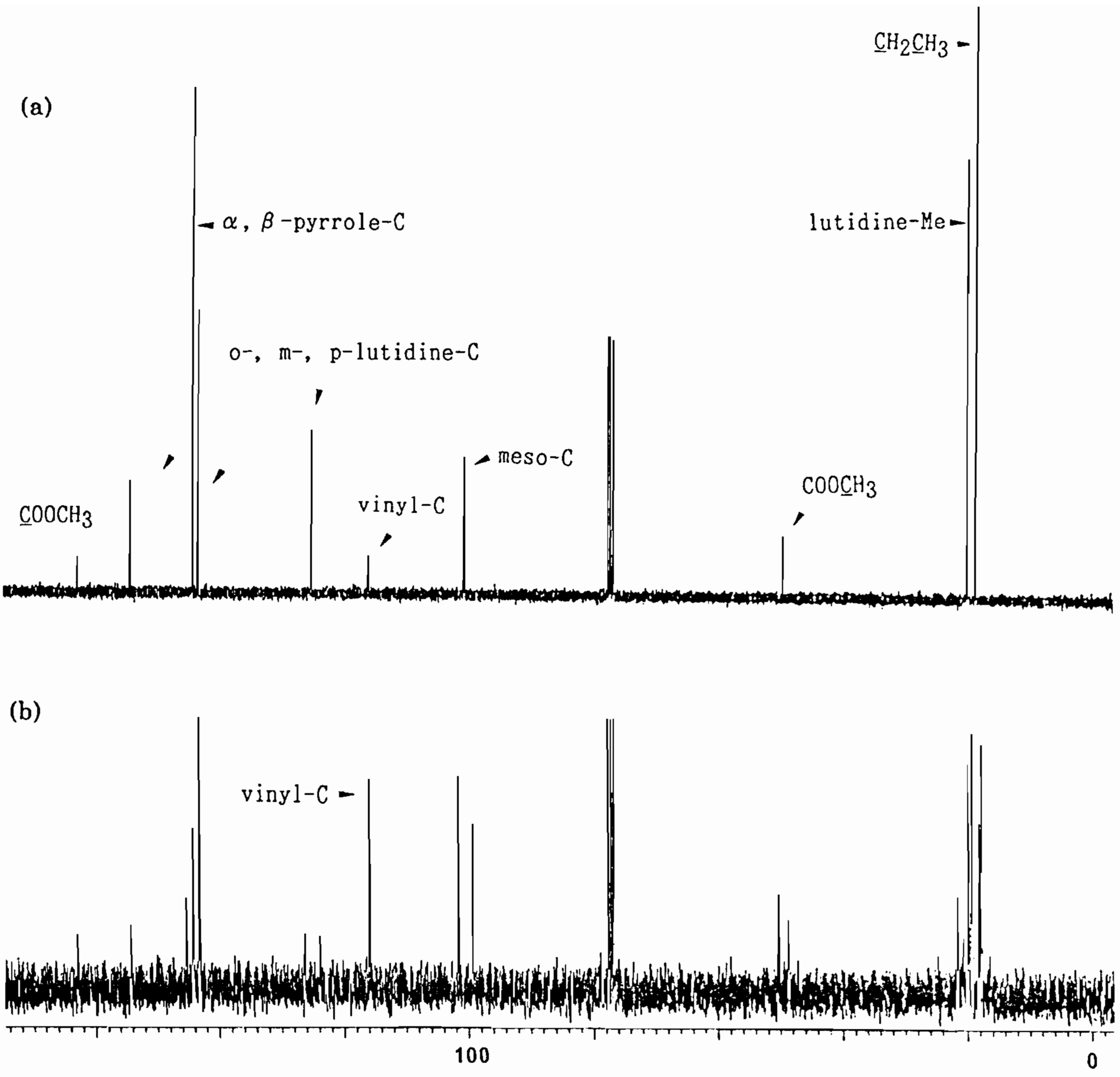


Figure 2-1. ^{13}C-NMR Spectra of **2b** by Proton Selective Decoupling at −1.22 ppm (a) and Proton Complete Decoupling (b)

Table 2-4. The ^{13}C-NMR Spectral Data of **2b** and **3b** (in $CDCl_3$)

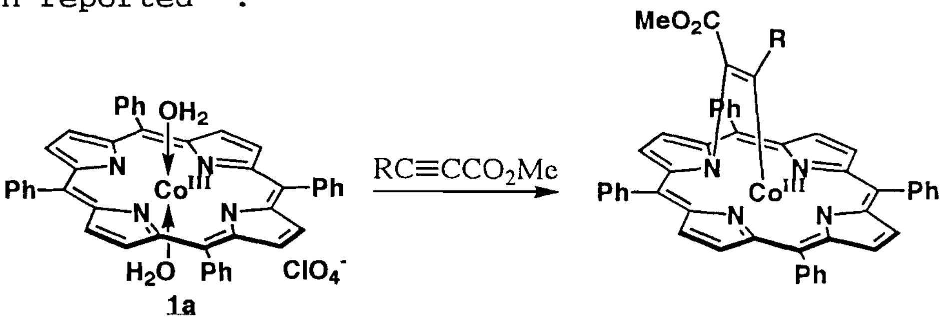
Compd.	Porphyrin Ligand			Others			
	meso	α,β-Py	CH_2CH_3	α[a]	β[a]	R[b]	2,6-Lutidine
2b	100.4	144.2 143.2	19.8 18.4	-	115.8	162.8, 49.4	154.2(*o*), 125.0(*m*) 144.0(*p*), 18.6(Me)
3b	99.8	144.4 142.9	19.8 18.3	-	133.6	128.5, 126.8 126.9, 127.4	152.8(*o*), 126.9(*m*) 144.4(*p*), 20.0(Me)

a) α and β denote Co−C= and Co−C=C− carbon, respectively.

b) Carbons due to substituents on the σ-vinyl group.

Reaction of Cationic Cobalt(III) Perchlorates in the Absence of a Bulky Amine

Acetylene dicarboxylic acid dimethyl ester and propiolic acid methyl ester also reacted with **1a** in the absence of a bulky amine to give *Co,N*-etheno bridged cobalt(III) porphyrins (**8**) and (**9**), respectively, with an acetylene triple bond inserted into a *Co,N*-bond in good yields. A similar reaction of **1b** has already been reported[1c].



1a

8; R = CO$_2$Me
9; R = H

Table 2-5. The ^{1}H-NMR Spectral Data of **8** and **9** (in CDCl$_3$)

Compd.	β-Pyrrole	Others
8	8.75(s,2H), 9.11(s,2H) 8.96(d,2H), 9.03(d,2H)	1.99, 2.63(s,3Hx2,CO$_2$CH$_3$)
9	8.77(s,2H), 9.34(s,2H) 7.80(d,2H), 8.95(d,2H)	2.01(s,3H,CO$_2$CH$_3$) 0.04(s,1H,Vinyl-H)

The UV-Vis spectra of **8**,**9** are similar to those of *Co,N*-methano-bridged cobalt(III) porphyrin complexes which have a relatively broad Soret band at 430 nm and a plateau-like Q-band centered at 550 nm. Compound **8** and **9** show the up-field shifted ^{1}H-NMR signals due to the bridge substituents as expected from the theory that the region over a porphyrin plane is magnetically anisotropic due to the porphyrin ring current effect. The singlet at 0.04 ppm in the ^{1}H-NMR spectrum of **9** is associated with the bridge vinylene proton which is observed at around -0.81 ppm in the case of *Co,N*-(methoxycarbonyletheno)(OEP)Co^{III}ClO$_4$. One factor attributed to this difference in the chemical shifts is the electron density of the conjugated π-system which are influenced by the peripheral substituents. ^{1}H-NMR spectra of **8** and **9** show two singlets and two doublets with equal intensity due to β-pyrrole protons of the porphyrin ring and three multiplets with 2:2:1 intensity due to *meso*-phenyl protons. This splitting pattern of the absorptions due to the porphyrin ring is consistent with the structure of C_s symmetry with a *Co,N*-bridging group. Two singlets at 1.99 and 2.63 ppm observed for **8** were tentatively assigned to the carbomethoxy groups on the cobalt and the nitrogen side, respectively, since the latter is expected to experience a smaller magnetic anisotoropy due to the ring current effect of porphyrin than the former.

Study on the Co^{III}-Alkyne Intermediate by UV-Vis, ^{1}H-NMR and ESR Spectral Data

Introduction of acetylene gas into (TTP)Co^{III}(H_2O)$_2$ClO$_4$ (**1c**) in CH_2Cl_2 solution resulted in the color change from red to green immediately. Addition of n-hexane to this reaction mixture gave precipitates that can be formulated as *N,N'*-vinylene linked bisporphyrin biscobalt(II) bisperchlorate (**10c**) on the basis of the spectral properties as shown below. The use of **1b** instead of **1c** gave acetylene complex **10b** in the same manner. UV-Vis spectral change recorded at one minute's interval after dissolution of **10b**, **c** in CH_2Cl_2 is shown in Figure 2-2 and Figure 2-3. **10c** which initially shows a Soret peak at 443 and Q-band peaks at 568, 622, and 667 nm almost identical with those of *N*-vinyl(TTP)Co^{II}OAc finally changed into **1c**. **10b** shows a more rapid spectral change than **10c**. The spectral change indicates that *N,N'*-vinylene bisporphyrin structure dissociates into acetylene and the corresponding cationic cobalt(III) porphyrin in CH_2Cl_2 solution.

^{1}H-NMR spectrum of **10b** in CD_2Cl_2 at 0°C shows two 2H-signals due to *meso* protons at 11.3 and -9.0 ppm which are absent in the spectrum of the *meso*-deuterated analogue, eight 2H-signals due to methylene protons at 38.1, 30.9, 30.3, 28.1, 23.0, 20.3 (overlapped), and 19.3 ppm, and four 6H-signals due to methyl protons

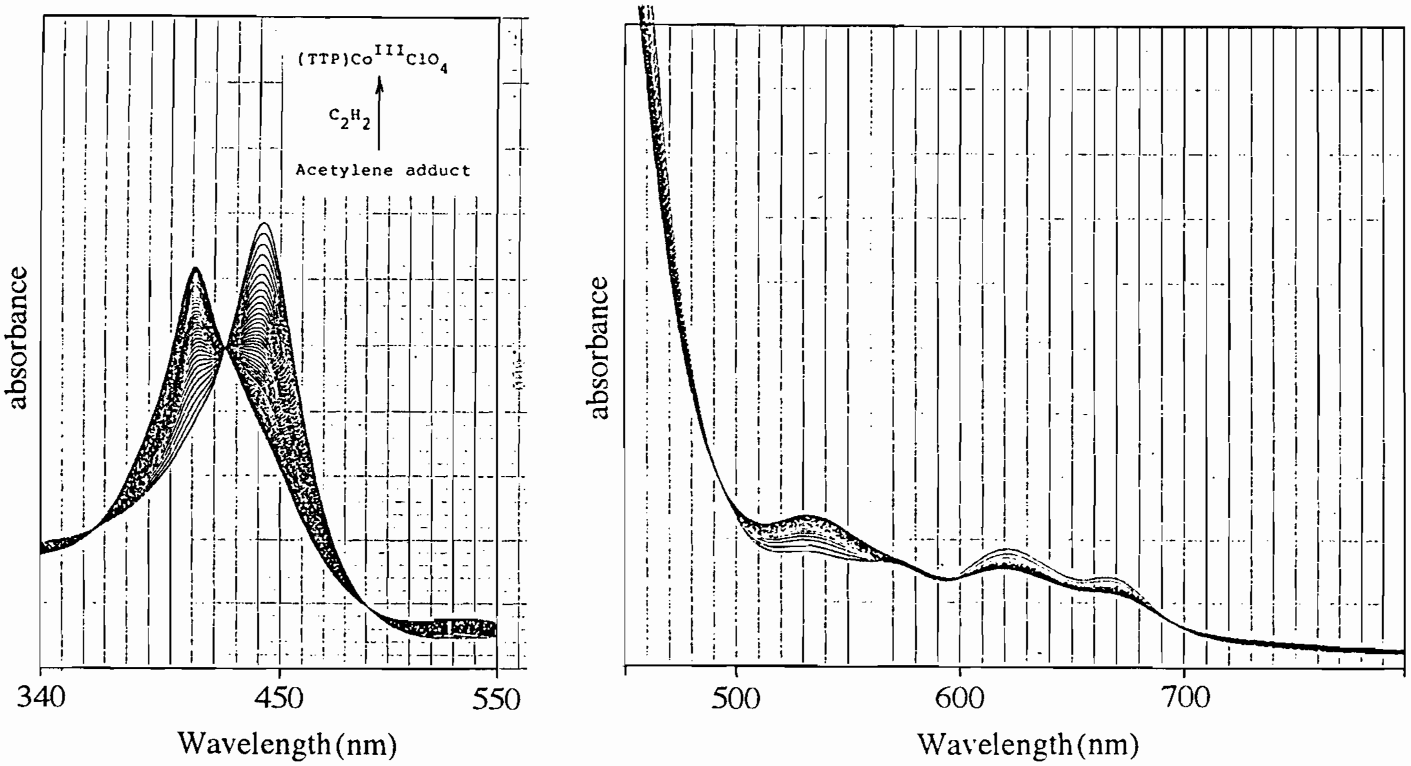


Figure 2-2. UV-Vis Spectral Change Recorded at One Minute's Intervals after Dissolution of **6c**

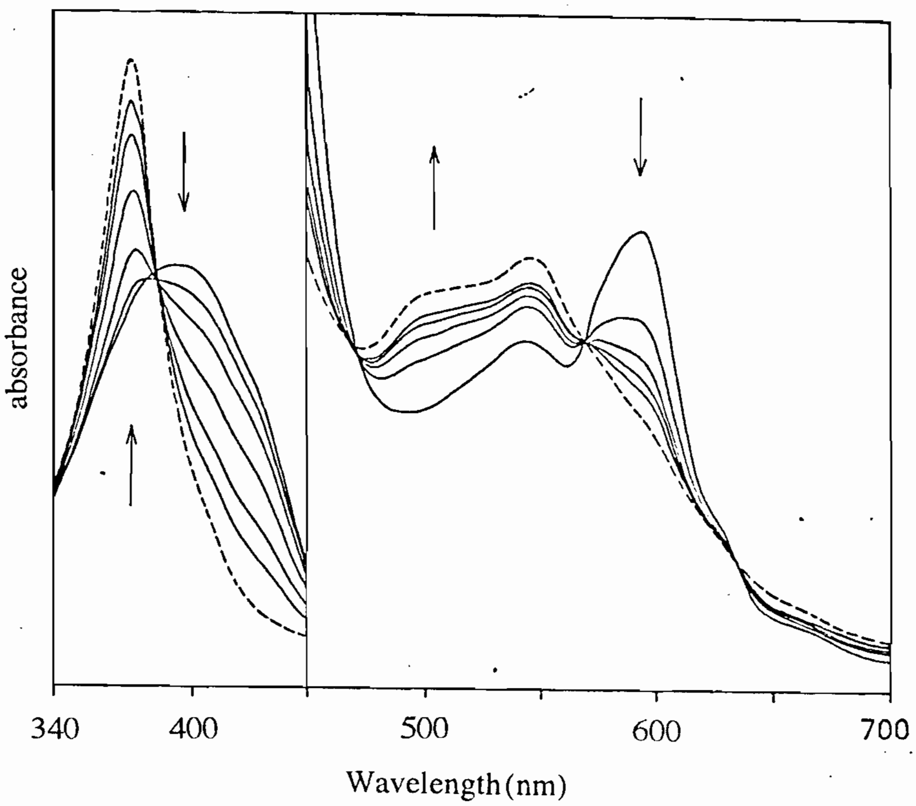


Figure 2-3. UV-Vis Spectral Change Recorded at One Minute's Intervals after Dissolution of **6b**

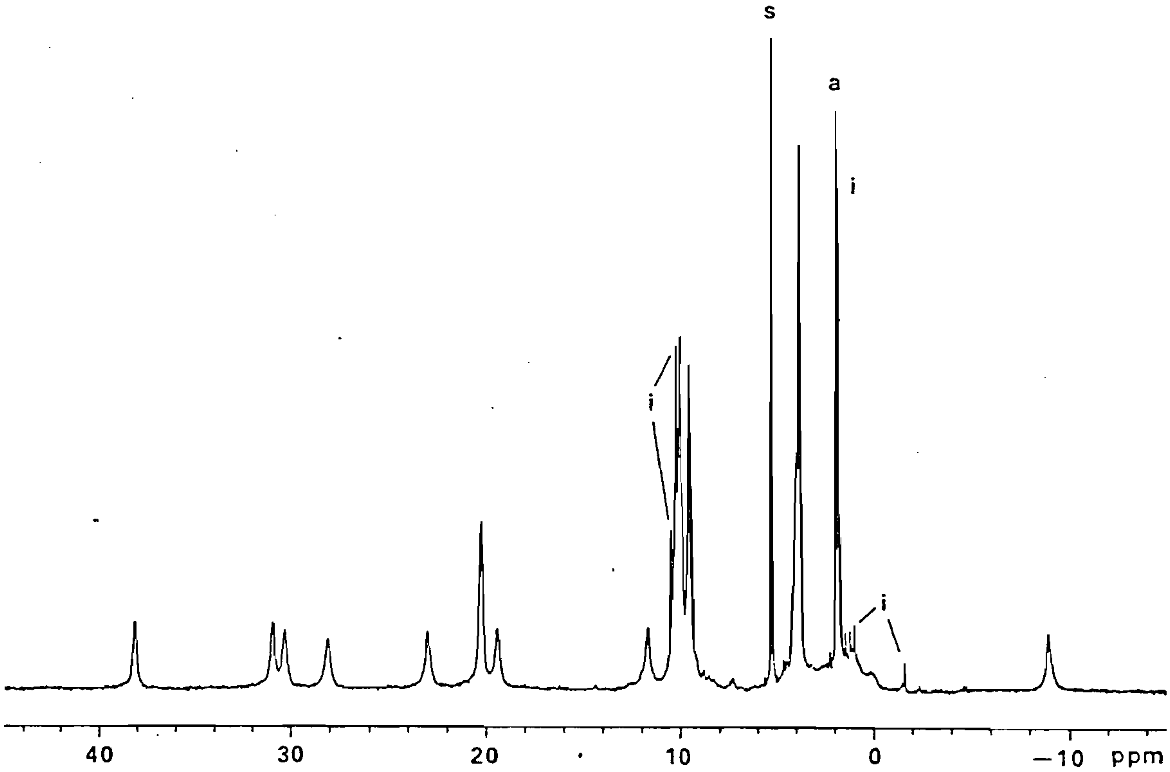


Figure 2-4. ^{1}H-NMR Spectrum of a Mixture of **1b** and Acetylene in CD_2Cl_2

at 10.2, 10.0, 9.5, and 3.9 ppm. However, signals derived from acetylene could not be recognized. The splitting pattern and chemical shifts range of this spectrum are quite similar to those of the d^7 high spin (S=3/2) N-Me(OEP)$Co^{II}OAc$[8]. In fact, the magnetic moment (μ_{eff}=5.2μB) of this acetylene adduct **10b** measured by the Evans method in $CDCl_3$ at 0 °C is not so different from the spin only value (3.87μB) for the d^7 high spin state (S=3/2). Although signals of **10c** could not be observed at all in the ^{1}H-NMR, treatment of **10c** with saturated NaSCN or KCl aqueous solution afforded stable *N*,*N*'-vinylene bisporphyrin complexes which could be characterized by ^{1}H-NMR, UV-Vis, and microanalysis (see Chapter III). Treatment of *N*,*N*'-vinylene-linked bisporphyrin biscobalt bischloride (see Chapter III) with $AgClO_4$ in CH_2Cl_2 resulted in the decomposition of the dimer structure to lead to 1c.

While ESR spectrum of **1** in CH_2Cl_2 solution shows a weak signal due to impurities of Co^{III} π-cation radical structure, frozen CH_2Cl_2 solution of **10b** and **10c** at 77 K showed intense ESR signals due to π-cation radicals with 14 G line width at g=2.00 and with 35 G line width at g=1.99, respectively, as shown in

Figure 2-5 and Figure 2-6. The intensity of the signal for **10b** decreased to 1% as the temperature was raised to 250 K, and then increased again to more than half of the original value as the temperature was lowered from 250 K to 77 K. These g-values at aroud **2** are indicative of a porphyrin π-cation radical.

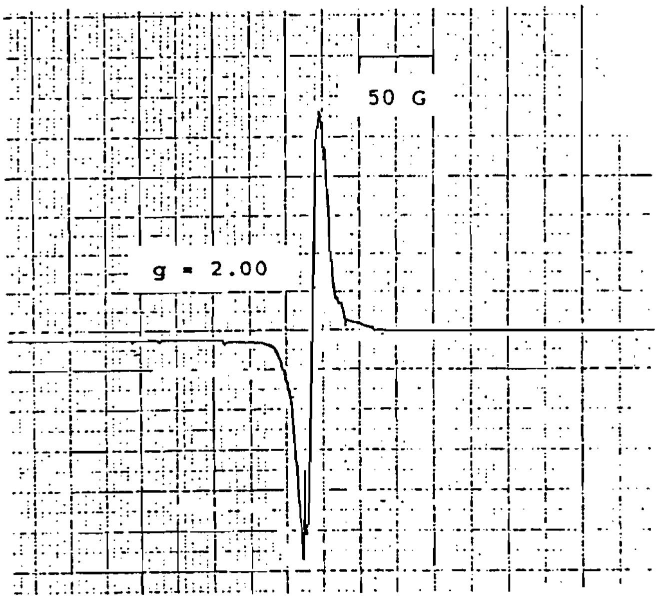


Figure 2-5. ESR Spectra of **6b** in Frozen CH_2Cl_2 at 77K

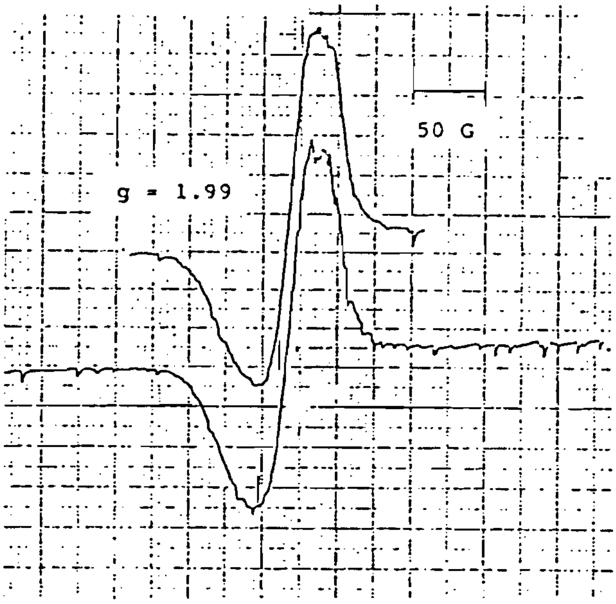


Figure 2-6. ESR Spectra of **6c** in Frozen CH_2Cl_2 at 77K

Moreover, ESR spectrum of **10b** in a microcrystalline stat at 4.2 K indicates signals at g=2.002 with 21 G line width, g=3 with 290G hyperfine coupling constant, and g=2.1 with 160G hyperfine coupling constant (see Figure 2-7). The latter two signals can be regarded as a perpendicular component and a parallel component of a low-spin cobalt(II) ion, respectively. It has been previously pointed out in a number of Co(II) porphyrin compounds that there is a linear relationship between the values of g-values and hyperfine coupling constants (A) and these parameter vary as the strength of axial ligands changes: four-, five-, and six-coordination.(see Figure 2-8)[9]. The ESR parameters determined in the present case conform well to this linear relationship and they are in the range indicative of tetragonal Co(II) coordination with a weak axial ligand effect. These ESR data are

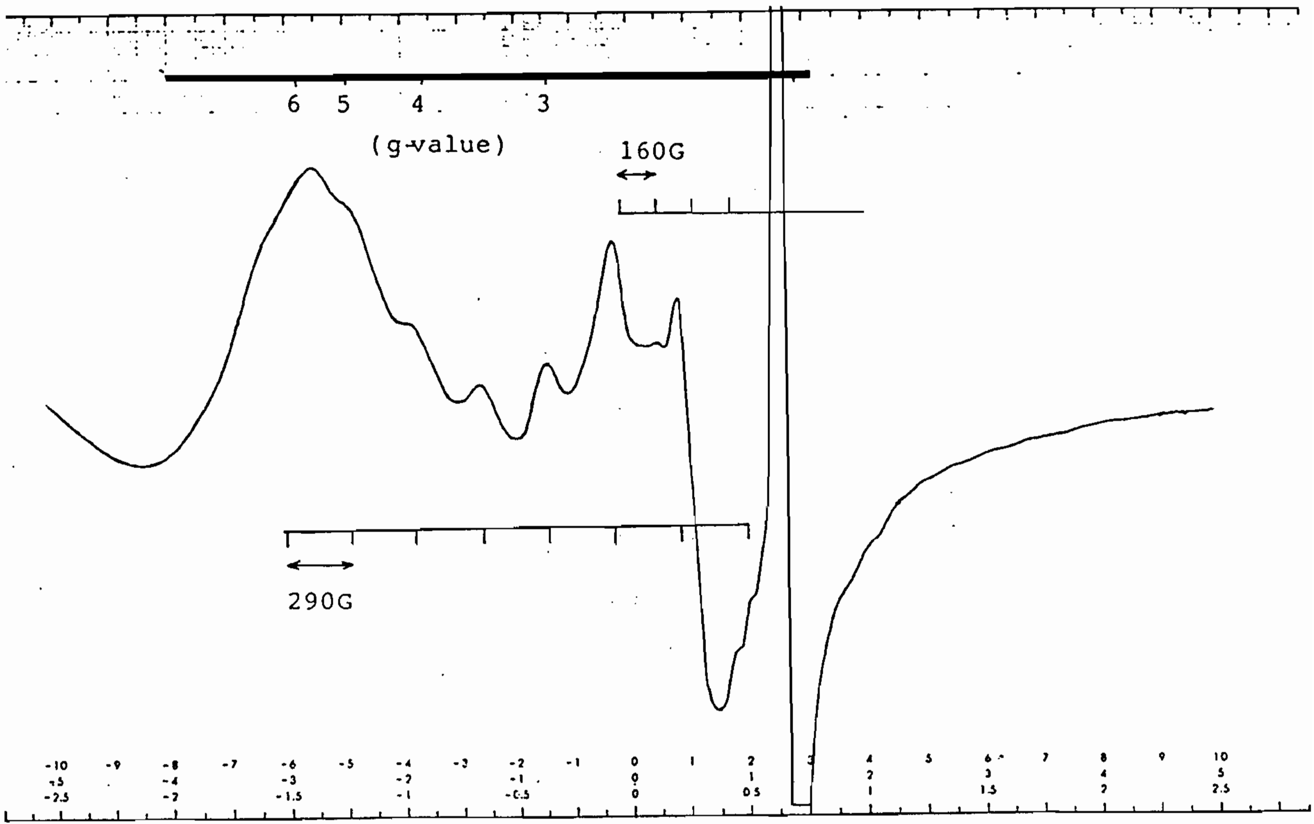
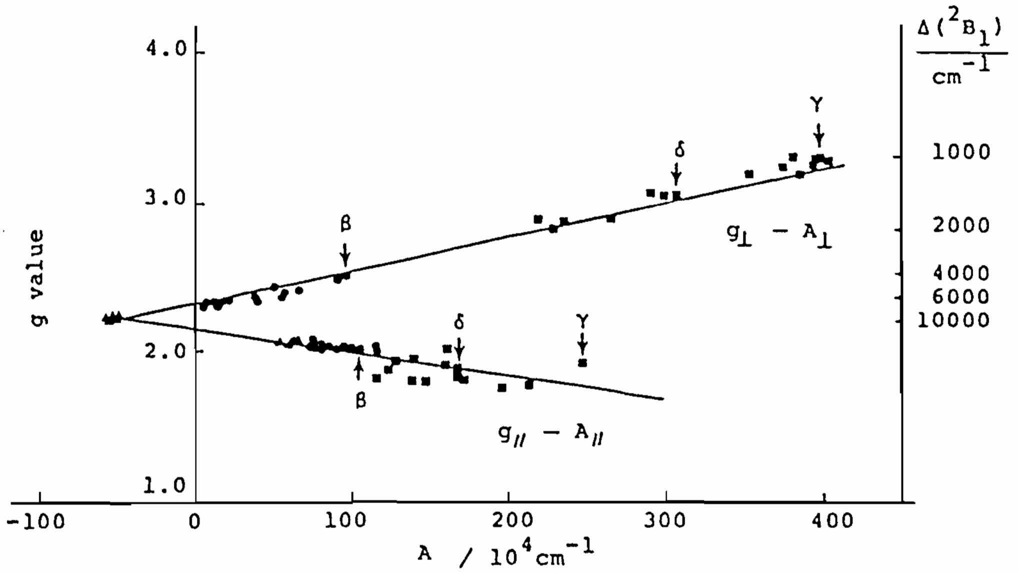


Figure 2–7. ESR Spectra of **6b** Powder at 4.2K



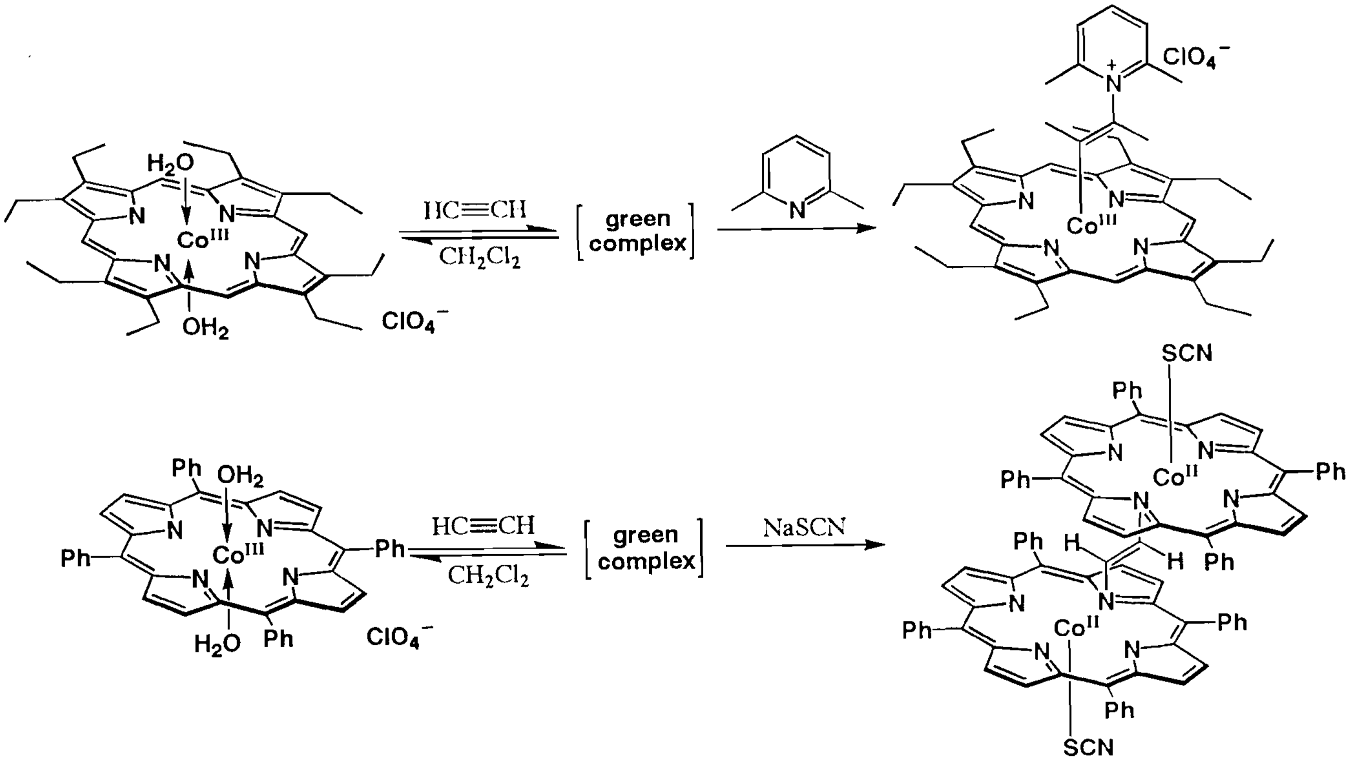
■: Four-coordinate complex, ●: five-coordinate complex, and ▲: six-coordinate complex.

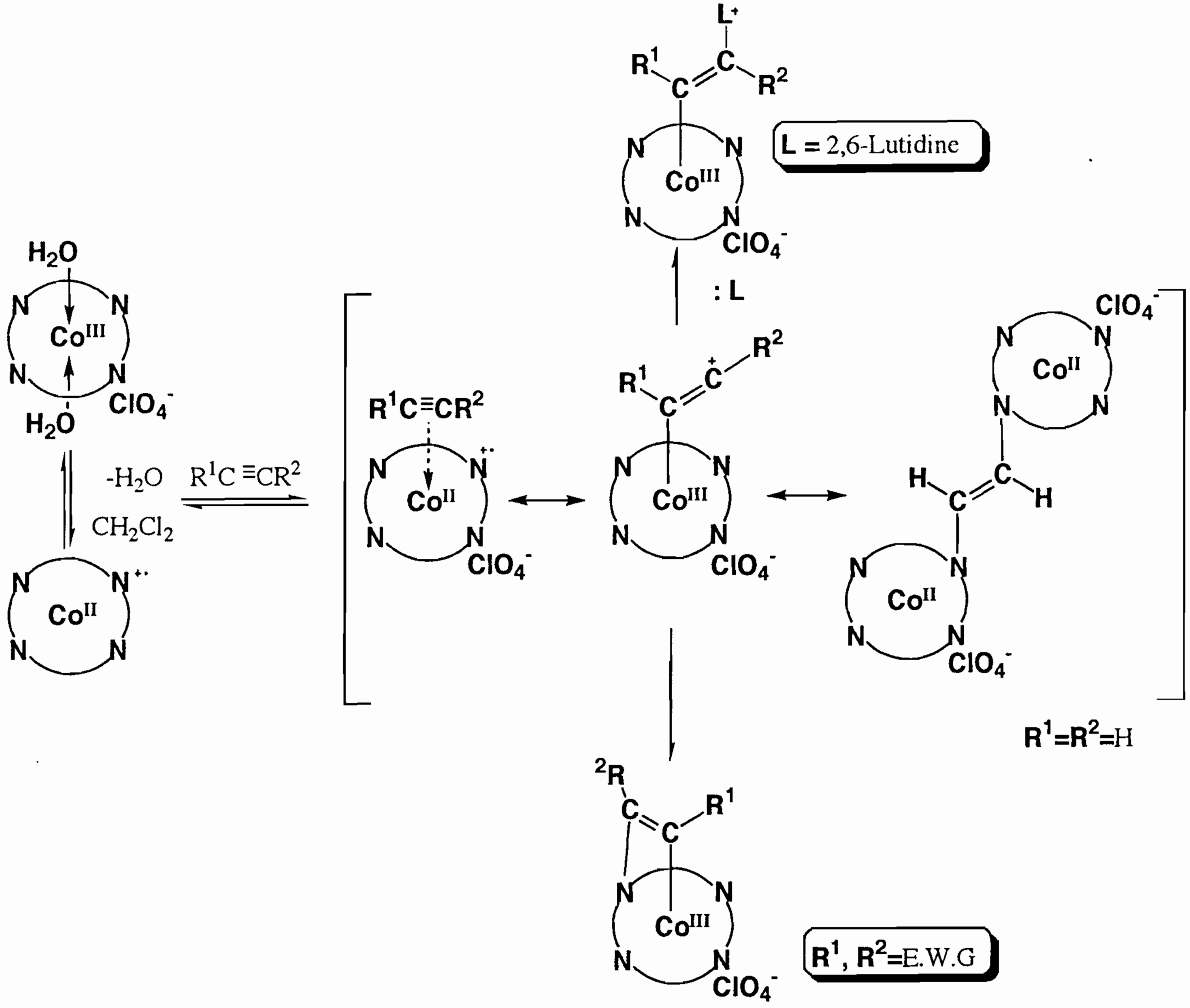
M. Kohno, H. Ohya-Nishiguchi, K. Yamamoto, T. Sakurai
Bull. Chem. Soc. Jpn., 57, 932 (1984).

Figure 2–8. A Correlation Diagram among *g*, *A* and Axial Ligation in Co^{II}

consistent with the formation of an acetylene π-complex of Co(II) porphyrin π-cation radical at low temperature. All the spectral data suggest that this reaction begins by the coordination of acetylene to the cobalt to give Co^{II}(porphyrin)acetylene π-complex intermediate which is then reversibly converted into *N*,*N*'-vinylene bisporphyrin biscobalt bisperchlorate.

The reasonable reaction mechanism is shown in Scheme 2-1. A cationic cobalt(III) porphyrin perchlorate releases weakly coordinating two water molecules to give Co^{II} porphyrin π-cation radical (**A**) in a non-polar solvent such as CH_2Cl_2. Co^{II} porphyrin π-cation radical binds acetylene derivatives to give (por)$Co^{+\bullet II}$ acetylene π-complex which is in the thermal equilibrium with *N*,*N*'-vinylene bisporphyrin (**B**) in the case of acetylene gas. Since substituted acetylenes also seem to give $(por)^{+\bullet}Co^{II}$ acetylene π-complexes, intermolecular nucleophilic attack of 2,6-lutidine occurs on the coordinated alkyne to give σ-(β-2,6-lutidiniumvinyl)cobalt(III) porphyrins. On the contrary, intramolecular nucleophilic attack of a pyrrolic nitrogen takes place in the absence of bulky amine to give *Co*,*N*-etheno bridged cobalt(III) porphyrins which could be isolated in the case of alkynes substituted with electron-attracting groups.





Scheme2-1 Reaction Mechanism

Table 2-6. The List of Elemental Analysis Data

Compd.	Formula		H	C	N
2a	$C_{55}H_{41}N_5O_6ClCo$	Found	4.28	70.03	9.48
		(Calc.)	(4.29)	(68.65)	(7.28)
4a	$C_{54}H_{41}N_5O_5ClCo$	Found	4.13	67.20	7.39
		(Calc.)	(4.13)	(67.20)	(7.39)
5a	$C_{61}H_{45}N_5O_6ClCo$	Found	4.78	69.54	6.24
		(Calc.)	(4.36)	(70.55)	(6.74)
6a	$C_{57}H_{43}N_5O_8ClCo$	Found	4.04	68.59	5.84
		(Calc.)	(4.25)	(67.10)	(6.86)
7a	$C_{53}H_{39}N_5O_4ClCo$	Found	4.25	69.95	7.48
		(Calc.)	(4.35)	(70.34)	(7.74)
2b	$C_{47}H_{57}N_5O_5ClCo$	Found	6.42	61.54	7.51
		(Calc.)	(6.51)	(63.98)	(7.94)
3b	$C_{51}H_{59}N_5O_4ClCo$	Found	6.74	67.45	7.65
		(Calc.)	(6.60)	(68.03)	(7.78)
4b	$C_{46}H_{57}N_5O_5ClCo$	Found	6.39	61.08	7.63
		(Calc.)	(6.72)	(64.67)	(8.20)
8	$C_{50}H_{34}N_4O_8ClCo$	Found	4.50	73.97	7.03
		(Calc.)	(3.75)	(65.76)	(6.14)

Experimental Section

General Comments. ^1H-, and ^{13}C-NMR spectra were recorded in deuteriochloroform by using a JEOL GX-270 spectrometer (270 MHz, 67.8 MHz), and ^1H-chemical shifts are referenced to tetramethylsilane, and ^{13}C-chemical shifts are measured relative to the signal of the solvent ($\delta(CDCl_3)$ 77.05 ppm). The coupling constants of pyrrolic and aromatic protons are in a normal range about 5 and 8 Hz, respectively, and will not be specified. UV-Vis spectra were taken in dichloromethane solution on a Shimadzu UV-240 or a Shimadzu UV-245Fs spectrometer. IR spectral measurements were made in a KBr disk with a Shimadzu IR-420 spectrometer. Elemental Analyses were performed on a Yanaco CHN MT2 recorder using acetanilide as a standard compound. Wakogel C-300 was used for silica gel column chromatography. Most reactions were monitored by using a Kieselgel 60F254 silica gel TLC plate.

Preparation of Cationic Cobalt(III) Porphyrin Perchlorate

$(TPP)Co^{III}(H_2O)_2ClO_4$ 1a; To suspension of $(TPP)Co^{II}$ (100 mg) in methanol (100 ml) was added 10% $HClO_4$ (1-2 ml) and the solution was stirred for about 12 hours to lead to almost complete dissolution. After the mixture was filtered and water (30 ml) was added, the solution was condensed under reduced pressure until fine crystals precipitated in water. The crystals were collected, washed with water, and dried in vacuum. Recrystallization from CH_2Cl_2-methanol afforded fine purple crystals.

$(OEP)Co^{III}(H_2O)_2ClO_4$ 1b; To a dry CH_2Cl_2 solution of $(OEP)Co^{II}$ was added a 3-fold excess of solid anhydrous $AgClO_4$ at room temperature and the mixture was stirred about one hour. The bright red solution of $(OEP)Co^{II}$ turns brown-red. The solution was then filtered and the products was isolated by precipitation with hexane followed by recrystallization from CH_2Cl_2-hexane.

Formation of σ-(β-2,6-Lutidiniumvinyl)Cobalt(III) Porphyrin

Perchlorates

General Procedure; A cationic cobalt(III) porphyrin (ca. 50 mg) was dissolved in CH_2Cl_2. Acetylene (ca. 3.5 eq.) was added to the mixture of 2,6-lutidine (ca. 5 eq.) and a cationic cobalt(III) porphyrin. After stirring for an hour at an ambient temperature, the reaction mixture was concentrated to a small volume by evaporation under vacuum. The solution was chromatographed on silica gel with CH_2Cl_2-acetone (10:1) to purify the desired product which could be collected as a second brown-red band. Recrystallization from CH_2Cl_2-hexane afforded σ-(β-2,6-lutidiniumvinyl)cobalt(III) porphyrins.

(TPP)Co^{III}-C(CO_2CH_3)=CH(C_7H_9N)ClO_4 2a; The reaction was performed by using (TPP)Co^{III}(H_2O)$_2$$ClO_4$ (**1a**) and propiolic acid methyl ester. According to the general procedure, compound **2a** was obtained in 58% yield: ^{1}H-NMR δ($CDCl_3$) 8.98 (singlet, 8H, β-pyrrole), 7.79x2, 8.16 (multipletx3, 20H, Ph-H), 0.39 (singlet, 3Hx2, Lutidine-Me), 6.62 (doublet, 1Hx2, *m*-lutidine), 7.38 (triplet, 1H, *p*-lutidine), 1.70 (singlet, 3H, CO_2CH_3), -0.21 (singlet, 1H, vinyl-H); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 407(5.06), 524(4.17), 553(4.36); Anal. Calcd for $C_{55}H_{41}N_5O_6ClCo$: C,68.65; H,4.29; N,7.28. Found. C,70.03; H,4.28; N,9.48.

(TPP)Co^{III}-CH=C(Ph)(C_7H_9N)ClO_4 3a; The reaction was performed by using (TPP)Co^{III}(H_2O)$_2$$ClO_4$ (**1a**) and phenyl acetylene. According to the general procedure, compound **3a** was obtained in 34% yield: ^{1}H-NMR δ($CDCl_3$) 8.89 (singlet, 8H, β-pyrrole), 7.76, 7.77, 8.02 (multipletx3, 24H, Ph-H), 0.49 (singlet, 3Hx2, lutidine-Me), 6.94 (doublet, 1Hx2, *m*-lutidine), 7.72 (triplet, 1H, *p*-lutidine), 0.20 (singlet, 1H, vinyl-H), 3.70 (doublet, 1Hx2, *o*-Ph), 6.73 (triplet, 1Hx2, *m*-Ph), 6.95 (triplet, 1H, *p*-Ph); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 430(5.06), 540(4.09); Anal. Calcd for $C_{59}H_{43}N_5O_4ClCo$: C,72.28; H,4.42; N,7.14.

(TPP)Co^{III}-CH=C(CH_2OH)(C_7H_9N)ClO_4 4a and **(TPP)Co^{III}-**

$C(CH_2OH)=CH(C_7H_9N)ClO_4$ 4a'; The reaction was performed by using (TPP)$Co^{III}(H_2O)_2ClO_4$ (**1a**) and propargyl alcohol. According to the general procedure, compound **4a** and **4a'** were obtained as a mixture in 9% total yield. **4a**: ^{1}H-NMR δ(CDCl$_3$) 8.95 (singlet, 8H, β-pyrrole), 7.76, 7.77, 8.10 (multipletx3, 20H, Ph-H), 0.49 (singlet, 3Hx2, lutidine-Me), 6.62 (doublet, 1Hx2, *m*-lutidine), 7.32 (triplet, 1H, *p*-lutidine), -0.31 (singlet, 1H, vinyl-H), -1.80 (doublet, 2H, CH_2OH), 0.24 (triplet, 1H, CH_2OH); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 422(5.06), 540(4.07); Anal. Calcd for $C_{54}H_{41}N_5O_5ClCo$: C,69.42; H,4.42; N,7.50. Found. C,67.20; H,4.13; N,7.39. **4a'**: ^{1}H-NMR δ(CDCl$_3$) 8.97 (singlet, 8H, b-pyrrole), 7.76, 7.77, 8.10 (multipletx3, 20H, Ph-H), 0.43 (singlet, 3Hx2, lutidine-Me), 6.62 (doublet, 1Hx2, *m*-lutidine), 7.32 (triplet, 1H, *p*-lutidine), -1.42 (singlet, 1H, vinyl-H), -0.15 (doublet, 2H, CH_2OH), 1.64 (triplet, 1H, CH_2OH)

(TPP)$Co^{III}-C(CO_2CH_3)=C(Ph)(C_7H_9N)ClO_4$ 5a; The reaction was performed by using (TPP)$Co^{III}(H_2O)_2ClO_4$ (**1a**) and phenyl acetylene. According to the general procedure, compound **5a** was obtained in 52% yield: ^{1}H-NMR δ(CDCl$_3$) 8.86 (singlet, 8H, β-pyrrole), 7.76, 7.78, 8.04 (multipletx3, 20H, Ph-H), 0.96 (singlet, 3Hx2, lutidine-Me), 6.90 (doublet, 1Hx2, *m*-lutidine), 7.56 (triplet, 1H, *p*-lutidine), 1.82 (singlet, 3H, CO_2CH_3), 4.08 (doublet, 1Hx2, bridge *o*-Ph), 6.88 (triplet, 1Hx2, bridge *m*-Ph), 7.13 (triplet, 1H, bridge *p*-Ph); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 435(4.96), 534(4.05); Anal. Calcd for $C_{61}H_{45}N_5O_6ClCo$: C,70.55; H,4.36; N,6.74. Found. C,69.54; H,4.78; N,6.24.

(TPP)$Co^{III}-C(CO_2CH_3)=C(CO_2CH_3)(C_7H_9N)ClO_4$ 6a; The reaction was performed by using (TPP)$Co^{III}(H_2O)_2ClO_4$ (**1a**) and acetylene dicarboxylic acid dimethyl ester. According to the general procedure, compound **6a** was obtained in 31% yield: ^{1}H-NMR δ(CDCl$_3$) 8.91 (singlet, 8H, β-pyrrole), 7.77, 7.79, 8.11 (multipletx3, 20H, Ph-H), 1.78, 2.42 (singletx2, 3Hx2, CO_2CH_3), 0.83 (singlet, 3Hx2, lutidine-Me), 7.17 (broad doublet, 1Hx2, *m*-lutidine), 7.65 (triplet, 1H, *p*-lutidine); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 412(5.11), 530(4.16); Anal. Calcd for $C_{57}H_{43}N_5O_8ClCo$: C,67.10; H,4.25; N,6.86. Found. C,68.59; H,4.04; N,5.84.

(TPP)Co^{III}-CH=CH(C_7H_9N)ClO_4 7a; The reaction was performed by using (TPP)Co^{III}(H_2O)$_2$$ClO_4$ (**1a**) and acetylene gas. According to the general procedure, compound **7a** was obtained in 14% yield: ^{1}H-NMR δ($CDCl_3$) 8.95 (singlet, 8H, β-pyrrole), 7.76, 7.78, 8.11(multipletx3, 20H, Ph-H), -0.06, 0.56 (singletx2, 1Hx2, vinyl-H, J_{trans}=13.1Hz), 0.27 (singlet, 3Hx2, lutidine-Me), 6.70 (doublet, 1Hx2, *m*-lutidine), 7.40 (triplet, 1H, *p*-lutidine); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 433(6.33), 548(5.07); Anal. Calcd?for $C_{53}H_{39}N_5O_4ClCo$: C,70.34; H,4.35; N,7.74. Found. C,69.95; H,4.25; N,7.48.

(OEP)Co^{III}-C(CO_2CH_3)=CH(C_7H_9N)ClO_4 2b; The reaction was performed by using (OEP)Co^{III}(H_2O)$_2$$ClO_4$ (**1b**) and propiolic acid methyl ester. According to the general procedure, compound **2b** was obtained in 77% yield: ^{1}H-NMR δ($CDCl_3$) 10.30 (singlet, 4H, *meso*-H), 4.06 (quartet, 16H, $C\underline{H}_2CH_3$), 1.88 (triplet, 24H, $CH_2C\underline{H}_3$), 0.09 (singlet, 3Hx2, lutidine-Me), 6.54 (doublet, 1Hx2, *m*-lutidine), 7.32 (triplet, 1H, *p*-lutidine), 1.44 (singlet, 3H, CO_2CH_3), -1.22 (singlet, 1H, vinyl-H); ^{13}C-NMR δ($CDCl_3$) 100.4 (*meso*-C), 143.2, 144.2 (α,β-pyrrole-C), 18.4, 19.8 (CH_2CH_3), 18.6 (lutidine-Me), 154.2, 125.0, 144.0 (*o*-, *m*-, *p*-lutidine-C), 115.8 (vinyl-C), 49.4 ($COO\underline{C}H_3$), 162.8 ($\underline{C}OOCH_3$); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 396(4.84), 552(4.22); Anal. Calcd for $C_{47}H_{57}N_5O_5ClCo$: C,63.98; H,6.51; N,7.94. Found. C,61.54; H,6.42; N,7.51.

(OEP)Co^{III}-CH=C(Ph)(C_7H_9N)ClO_4 3b; The reaction was performed by using (OEP)Co^{III}(H_2O)$_2$$ClO_4$ (**1b**) and phenyl acetylene. According to the general procedure, compound **3b** was obtained in 49% yield: ^{1}H-NMR δ($CDCl_3$) 10.07 (singlet, 4H, *meso*-H), 3.99 (quartet, 16H, $C\underline{H}_2CH_3$), 1.84 (triplet, 24H, $CH_2C\underline{H}_3$), 0.20 (singlet, 3Hx2, lutidine-Me), 6.77 (doublet, 1Hx2, *m*-lutidine), 7.59 (triplet, 1H, *p*-lutidine), -0.51 (singlet, 1H, vinyl-H), 3.64 (doublet, 1Hx2, bridge *o*-Ph), 6.55 (triplet, 1Hx2, bridge *m*-Ph), 6.86 (triplet, 1H, bridge *p*-Ph); ^{13}C-NMR δ($CDCl_3$) 99.8 (*meso*-C), 142.9, 144.4 (α,β-pyrrole-C), 18.3, 19.8 (CH_2CH_3), 20.0 (lutidine-Me), 152.8, 126.4, 144.4 (*o*-, *m*-, *p*-lutidine-C), 133.6 (vinyl-C), 128.5, 126.8, 126.9, 127.4 (bridge Ph-C); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 399(5.68), 554(5.16); Anal. Calcd for $C_{51}H_{59}N_5O_4ClCo$: C,68.03; H,6.60; N,7.78. Found. C,67.45; H,6.74; N,7.65.

(OEP)Co^{III}-CH=C(CH_2OH)(C_7H_9N)ClO_4 4b and **(OEP)Co^{III}-C(CH_2OH)=CH(C_7H_9N)ClO_4 4b'**; The reaction was performed by using (OEP)Co^{III}(H_2O)$_2ClO_4$ (**1b**) and propargyl alcohol. According to the general procedure, compound **4b** and **4b'** were obtained as a mixture in 30% total yield. **4b:** ^{1}H-NMR δ($CDCl_3$); 10.27 (singlet, 4H, *meso*-H), 4.07 (quartet, 16H, CH_2CH_3), 1.87 (triplet, 24H, CH_2CH_3), 0.13 (singlet, 3Hx2, lutidine-Me), 6.51 (doublet, 1Hx2, *m*-lutidine), 7.22 (triplet, 1H, *p*-lutidine), -0.89 (singlet, 1H, vinyl-H), -2.47 (doublet, 2H, CH_2OH), -1.03 (triplet, 1H, CH_2OH); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 396(4.84), 552(4.22); Anal. Calcd for $C_{46}H_{57}N_5O_5ClCo$: C,64.67; H,6.72; N,8.20. Found. C,61.08; H,6.39; N,7.63. **4b':** ^{1}H-NMR δ($CDCl_3$) 10.15 (singlet, 4H, *meso*-H), 4.03 (quartet, 16H, CH_2CH_3), 1.84 (triplet, 24H, CH_2CH_3), 0.16 (singlet, 3Hx2, lutidine-Me), 6.50 (doublet, 1Hx2, *m*-lutidine), 7.22 (triplet, 1H, *p*-lutidine), -1.99 (singlet, 1H, vinyl-H), -0.68 (doublet, 2H, CH_2OH), 0.77 (triplet, 1H, CH_2OH)

Preparation of *Co,N*-Etheno Bridged Cobalt(III) Porphyrin Perchlorates

***Co,N*-(H_3COCOC=$CCOOCH_3$)(TPP)Co^{III}ClO_4 8**; To (TPP)Co^{III}(H_2O)$_2ClO_4$ (1a) (ca. 50 mg) dissolved in CH_2Cl_2, acetylene dicarboxylic acid dimethyl ester (ca. 3.5 eq.) was added. After stirring for an hour at an ambient temperature, the reaction mixture was concentrated to a small volume by evaporation under vacuum. The solution was chromatographed on silica gel with CH_2Cl_2-acetone (10:1) to purify the desired product which could be collected as a brown-green band. Recrystallization from CH_2Cl_2-hexane afforded **4** in 82% yield: ^{1}H-NMR δ($CDCl_3$) 8.75, 9.11, 8.96, 9.03 (singletx2, doubletx2, 2Hx4, β-pyrrole), 7.6~8.4 (multiplet, 20H, *meso*-Ph), 1.99, 2.63 (singletx2, 3Hx2, CO_2CH_3); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 430(4.79), 588(3.54); Anal. Calcd for $C_{50}H_{34}N_4O_8ClCo$: C,65.76; H,3.75; N,6.14. Found. C,73.97; H,4.50; N,7.03.

***Co,N*-(HC=CCOOCH$_3$)(TPP)Co^{III}ClO$_4$** **9**; (TPP)Co^{III}(H$_2$O)$_2$ClO$_4$ (**1a**) (ca. 2.3 mg) and methyl propiolate (ca. 0.24 ml) were dissolved in $CDCl_3$, and then ^{1}H-NMR spectrum was measured: ^{1}H-NMR δ($CDCl_3$) 8.77, 9.32, 7.80, 8.95 (singletx2,doubletx2, 2Hx4, β-pyrrole), 7.4~8.4 (multiplet, 20H, *meso*-Ph), 0.04 (singlet, 1H, vinyl-H), 2.01 (singlet, 3H, CO_2CH_3)

Preparation of acetylene complexes

Cationic cobalt(III) porphyrin perchlorate (ca. 50 mg) was dissolved dry CH_2Cl_2 (ca. 5 ml). Purified acetylene gas was bubbled into this solution. The color of the solution changed from brown-red to green immediately. The reaction mixture was stirred for addition five minutes under an acetylene atmosphere. Additional of n-hexane with simultaneous removal of CH_2Cl_2 on the hot plate afforded precipitates. The solvent was filtered off and the precipitates was dried in vacuo.

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Chapter III

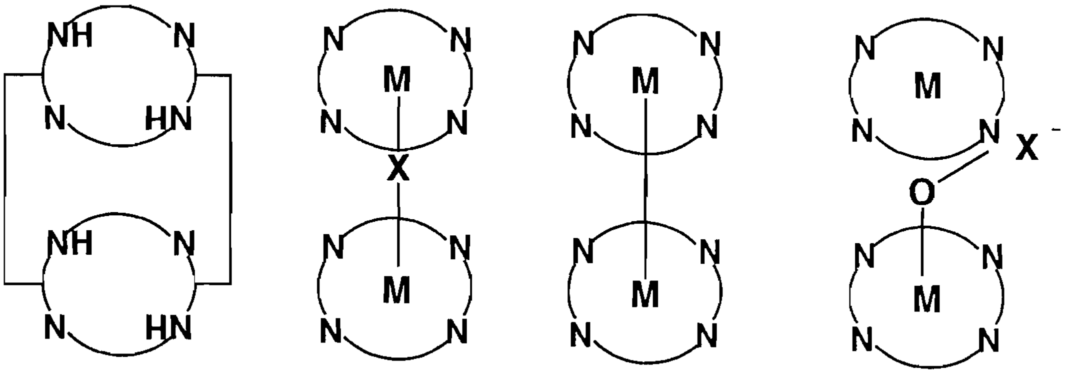
Syntheses and Properties of *N*,*N*'-, and *Co*,*N*'-Vinylene-Linked Bisporphyrins; New Dimeric Porphyrin Structure related to Chlorophyll Dimer

Summary

Bis(aquo)*meso*-tetraphenylporphyrinatocobalt(III) perchlorate, (TPP)$Co^{III}(H_2O)_2ClO_4$ (**1a**), and bis(aquo)*meso*-tetra(*p*-tolyl)porphyrinatocobalt(III) perchlorate, (TTP)$Co^{III}(H_2O)_2ClO_4$ (**1b**), which give Co^{II} porphyrin π-cation radicals in non-polar solvents, reacted immediately with acetylene gas, in the absence and presence of the corresponding cobalt(II) porphyrins, to give directly *N,N'*-vinylene-linked bisporphyrin biscobalt(II) complexes (**2a,b**) and *Co,N'*-vinylene-linked bisporphyrin cobalt(III) hydroperchlorate complexes (**6a,b**), respectively. The Co^{II} ions of **2b** could be easily replaced with Fe^{II} and Zn^{II} ions by way of the corresponding free base (**3b**) which was generated from **2b** by demetallation with trifluoroacetic acid, or from **6b** by oxidative rearrangement. **6b** was metallated easily by Fe^{II} and Zn^{II} ion via its free base which was afforded with chromatography on alumina. The labile adduct complex obtained from 1a and (OEP)$Co^{III}(H_2O)_2ClO_4$ (1c) with acetylene gas reacted immediately also with porphyrin free bases such as $OEPH_2$, $TTPH_2$ to give *Co,N'*-vinylene bisporphyrins. Spectral properties and redox behaviors of these layered porphyrins are to be reported.

Introduction

Covalently linked bisporphyrins with layered structure have been the focus of recent studies directed to develop artificial molecular system with functions based on their layered structure, and have only recently become significant in this context. These bisporphyrin systems so far identified can be classified into four groups on the basis of their structure. The first class is bisporphyrins linked through peripheral substitution[1], which is regarded as model compounds for the reaction center chlorophyll dimer, the second class is bisporphyrins linked with axial coordination[2] such as oxygen, nitrogen and so on, the third class is bisporphyrins which have a metal-metal bonding[3], and the last class is a bisporphyrin in which an oxygen atom bridges a pyrrolic nitrogen to the central metal[4]. Until our work[5], the last one has been the only one example of bisporphyrin based on the N-substitution. Especially catena-μ-ethynylene phthalocyaninatocobalt(III)[6] arrested attention to its expected conductivity. This chapter describes the first synthesis of *N,N'*- and *Co,N'*-vinylene-linked bisporphyrins through novel and easy organometallic reactions of cationic cobalt(III) porphyrins with acetylene gas.



Scheme 3-1 Layered Bisporphyrins

Results and Discussion

Syntheses and Properties of *N,N'*-Vinylene Bisporphyrins

Bis(aquo)*meso*-tetraphenylporphyrinatocobalt(III) perchlorate, (TPP)$Co^{III}(H_2O)_2ClO_4$ (**1a**), and bis(aquo)*meso*-tetra(*p*-tolyl)porphyrinatocobalt(III) perchlorate, (TTP)$Co^{III}(H_2O)_2ClO_4$ (**1b**), which give Co^{II} porphyrin π-cation radicals in non-polar solvents, reacted immediately with acetylene gas in CH_2Cl_2 solution showing a color change from red to green. Work-up with saturated NaSCN aqueous solution followed by chromatography on silica gel with CH_2Cl_2 gave a stable complex (**2a,b**) in 48% and 60% yields, respectively. Work up with saturated KCl aqueous solution followed by chromatography on silica gel with CH_2Cl_2-acetone (10:1) could afford the corresponding chloride complex (**2b'**) in 56% yield.

The UV-Vis spectra of **2** are virtually the same as that of *N*-(CH=CHCl)TTPCo^{III}SCN (**A**) which shows a Soret band at about 450 nm and a three-banded Q-band (so called Rhodo type) (see Chapter I).

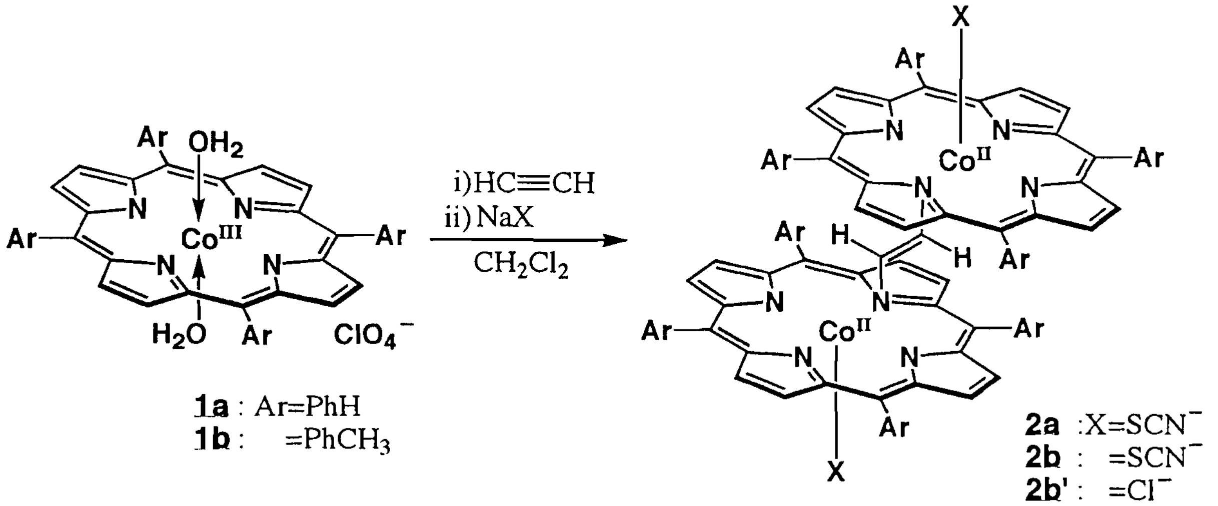


Table 3-1. λ_{max} Values of *N,N'*-Vinylene-Linked Bisporphyrins **2a-2b** (in CH_2Cl_2)

Compd.	λ_{max} Value(log ε)			
2a	442(5.33),	567(4.07),	618(4.00),	661(4.00)
2b	445(5.92),	570(4.06),	621(4.21),	666(4.03)
2a'				
2b'	442(5.27),	544(4.12),	618(4.13),	665(3.95)

Compound **2** shows a well resolved paramagnetic ^{1}H-NMR spectrum with a C_s symmetric pattern which is characteristic of a *N*-substituted porphyrin. In this case, there are four distinct β-pyrrole signals, and two sets of *meso*-aryl signals. It is expected that the two ortho and two meta positions on each *meso*-aryl ring are distinguishable due to the restricted rotation around the *meso*-carbon-to-phenyl bond. A detailed comparison of the ^{1}H-NMR spectra between **2a,b**, a d_8-TPP analogue (deuteriated at the pyrrole β-positions) and **A** allowed us to assign β-pyrrole protons, and *o*-, *m*-, and *p*- protons of *meso*-aryl substituents. A set of signals at 41.8, 40.20, 33.8, and -3.4 ppm are associated to β-pyrrole protons, 20.8, 16.3, 9.5, and -0.6 ppm to *o*-phenyl protons, 15.4, 13.9, 11.8, and 5.8 ppm to *m*-phenyl protons, and 9.5, 8.7 ppm to *p*-phenyl protons for **2a**. A resonance peak of vinylene protons could be detected at about -170 ppm. In the case of **A**, one set of a broad peak due to the α-vinyl proton and a

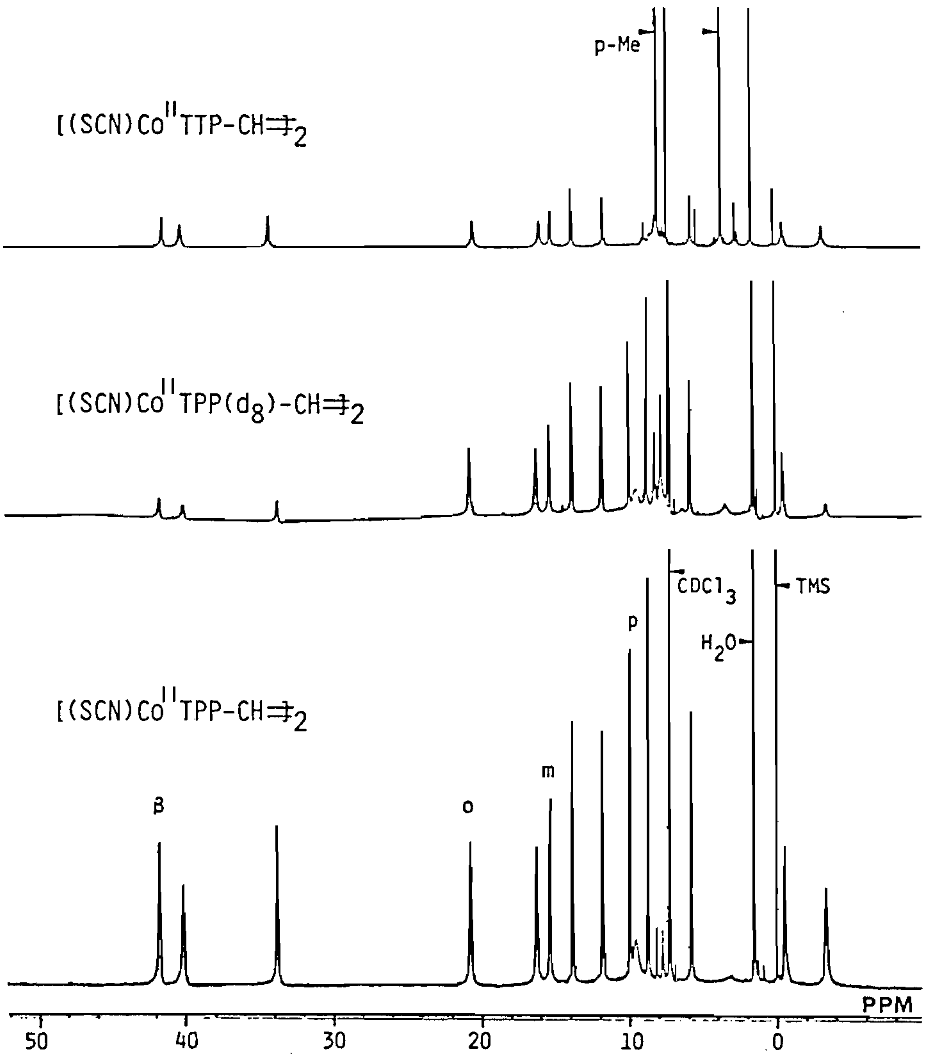


Figure 3-1. Paramagnetic ^{1}H-NMR Spectra of *N*,*N'*-Vinylene Bisporphyrin Complexes

Table 3-2. The ^{1}H-NMR Spectral Data and The Yields of **2a**, **2b**, and **2b'** (in CDCl$_3$)

Compd.	Porphyrin Ligand				Other	Yield
	β-Pyrrole	*o*-	*m*-	*p*-	Vinyl	(%)
2a	41.8,40.2 33.8,-3.4	20.8,16.3 9.5,-0.6	15.4,13.9 11.8, 5.8	9.5 8.7		48
2b	41.5,40.3 34.3,-3.3	20.4,15.9 8.8,-0.6	15.2,13.7 11.6, 5.6	7.9 3.6	-178	60
2b'	48.1,39.5 36.8,-8.4	20.1,18.1 5.4, 1.1	14.3,14.0 11.7, 6.1	7.7 3.8		56

sharp peak due to the β-vinyl proton are observed at -69.6 and -95.1 ppm, respectively. Each vinyl protons of **2a** is subjected to the magnetic effect of two cobalt porphyrin moieties at the same time, because the sum of the chemical shift of the α-vinyl proton and that of the β-vinyl proton of **A** gives -164.7 ppm, of which value is almost the same size as the shift of the vinylene protons of **2a**.

A Curie plot[7] for the β-pyrrole and the *meso*-aryl resonances of **2a** is given in Figure 3-2. The experimental data show linear relationship and the extrapolated intercepts come close to the chemical shifts of the diamagnetic reference compound, *N*,*N*'-(CH=CH)(TPPZn^{II}Cl)$_2$ (**5a**). This indicates that the spin state of **2a** is not varied throught the temperature range examined. The value of the magnetic moment is given by the following equation.

$$\mu_B = 2.828\sqrt{T\chi_M} \quad \text{------------------} \quad (1)$$

Where χ_M is molar magnetic susceptibility. When ΔH is the chemical shift difference between the internal standard and the external standard in the ^{1}H-NMR spectra, χ_M is expressed as function of C(concentration) and ΔH as shown by the following equation.

$$\chi_M = \frac{3\times10^3}{2\pi C}\frac{\Delta H}{H} \quad \text{------------------} \quad (2)$$

Then the value of μ is estimated by the above equations. μ_B is also theoretically correlated with spin quantum number.

$$\mu_B = \sqrt{S(S+1)} \quad \text{------------------} \quad (3)$$

If the magnetic interaction between two paramagnetic centers would be negligible, the value of magnetic moment of dinuclear system is given by the following.

$$\mu = \sqrt{\mu_a^2+\mu_b^2} \quad \text{------------------} \quad (4)$$

The magnetic moments (5.1 μ_B and 4.8 μ_B) measured by Evans method[9] in $CDCl_3$ at 30 °C clearly show that these complexes have two d^7 high spin state Co^{II} for which the theoretical magnetic

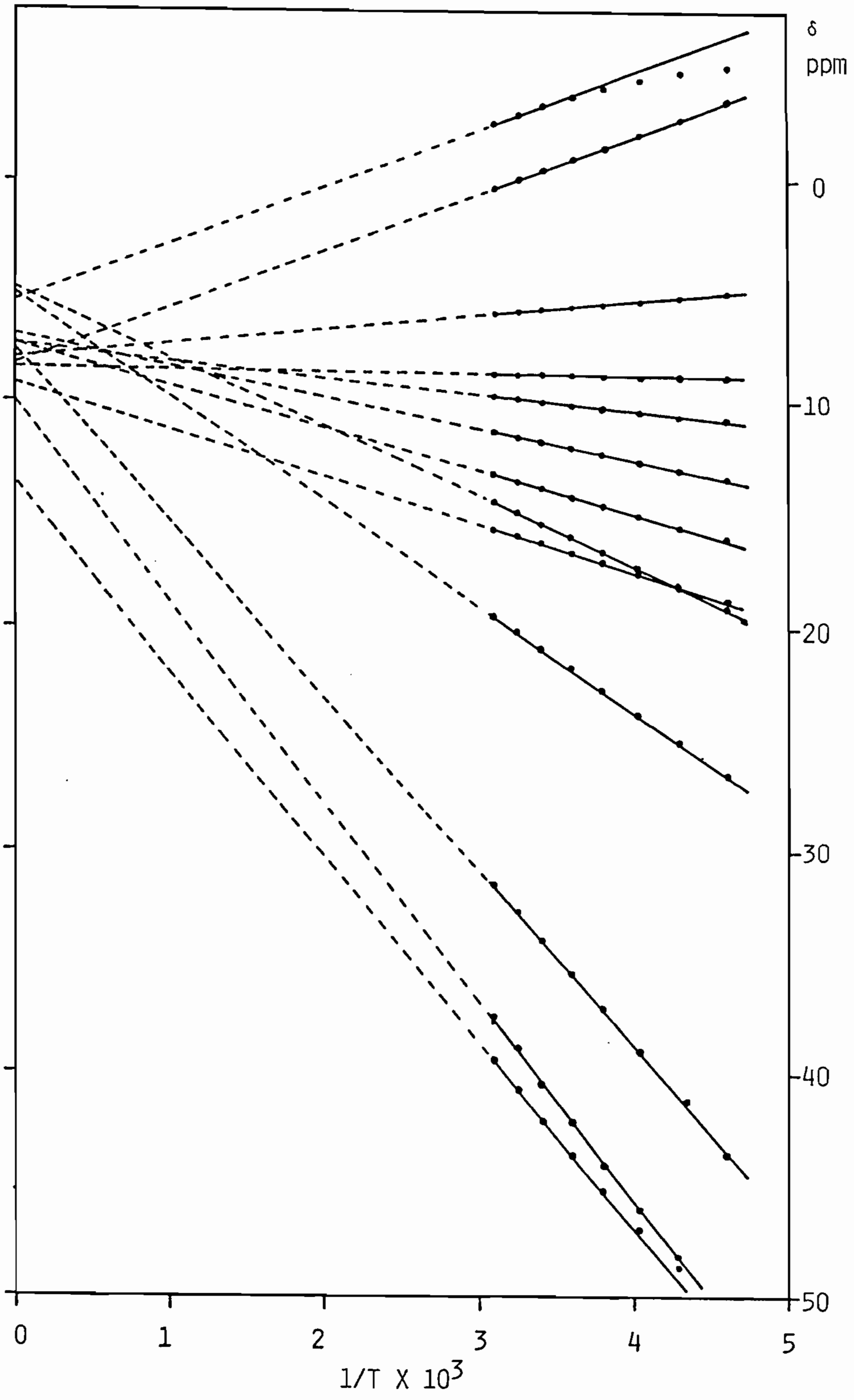
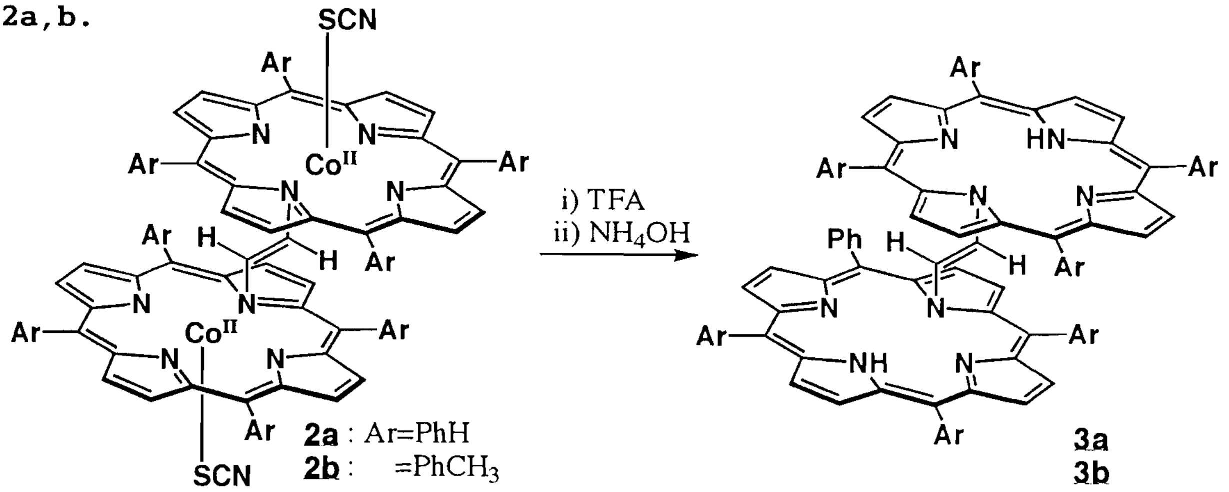


Figure 3-2. Curie Plots of *N,N'*–Vinylene Bisporphyrin Complex of **2**

moment is estimated to be 5.5 μ_B as a non-interacting spin only value[8] and that they are made up of two parts of porphyrin and one part of acetylene. These data are consistent with the *N,N'*-vinylene bisporphyrin biscobalt bisthiocyanate structure for 2a,b.



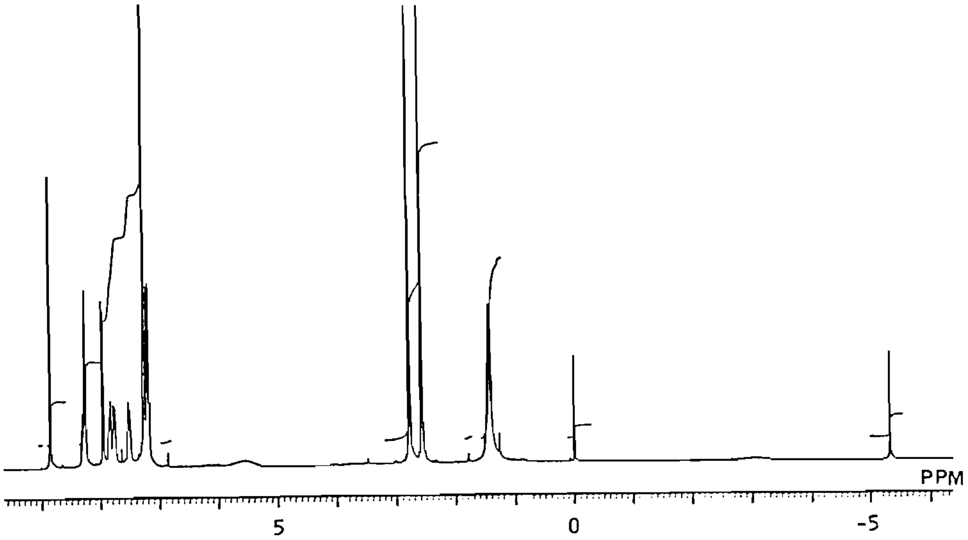


Figure 3-3. ^{1}H-NMR Spectra of *N,N'*-Vinylene Bisporphyrin Free Base of **3b**

Table 3-4. The ^{1}H-NMR Spectral Data of **3a**-**3b** (in $CDCl_3$)

Compd.	Porphyrin Ligand Other					Vinyl
	β-Pyrrole	*o*-	*m*-	*p*-	NH	
3a	8.86, 8.27				-3.1	-5.32
	7.96, 6.08		8.5-5.4			
3b	8.86, 8.26			2.79*	-3.1	-5.33
	7.96, 6.08		8.3-5.4	2.57*		

*) The signal intensity is 3H

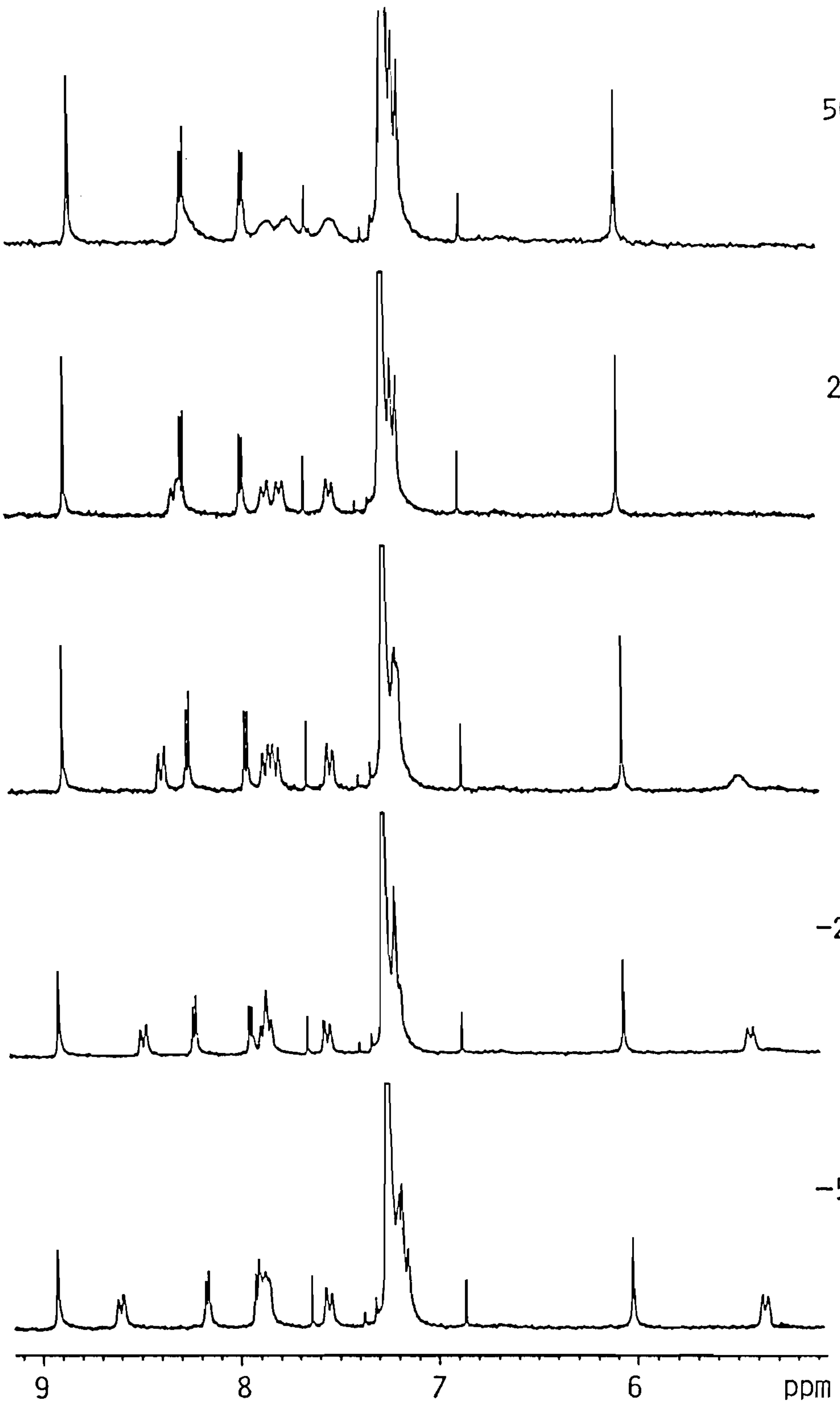
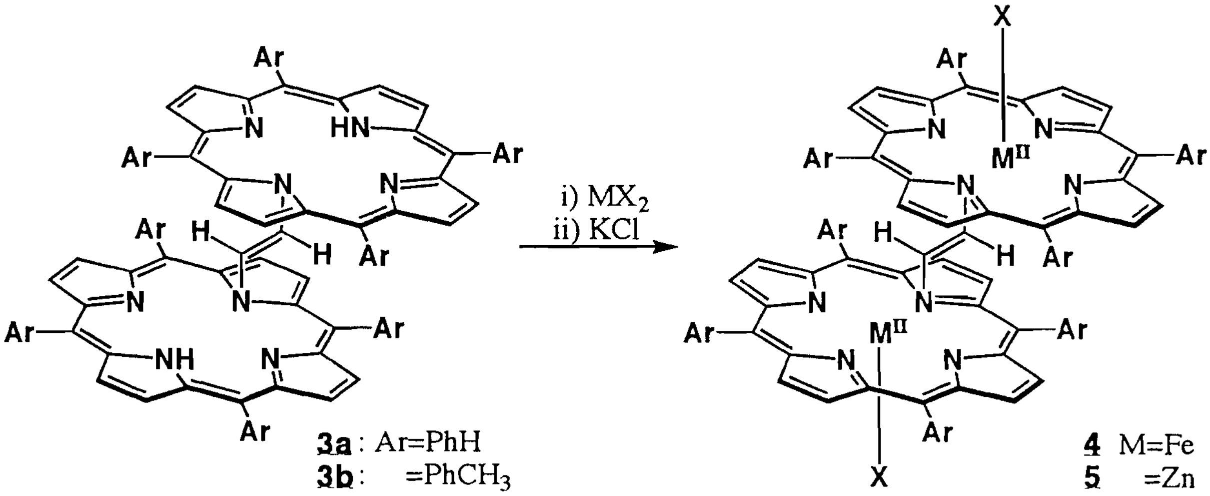


Figure 3-4. Variable Temperature ^{1}H-NMR Spectra of the Aromatic Region of *N,N'*-Vinylene Bisporphyrin Free Base **3**

Demetallation of **2a,b** with trifluoroacetic acid in CH_2Cl_2 for 15 minutes at ambient temperature followed by neutralization with aqueous ammonia gave *N,N'*-vinylene bisporphyrin free base (**3a,b**), respectively, in good yield. The unusually up-field shifted ^{1}H-NMR signals at 0 °C associated with *N,N'*-vinylene protons at -5.33 ppm, pyrrole-protons at 6.06 ppm, and *meso* ortho-phenyl rotons at 5.31 ppm and the remarkable temperature dependent line broadening of the *meso*-aryl resonances caused by the restricted rotation around a *meso*-carbon-to-phenyl bond provide the best evidence in support of the *N,N'*-vinylene-linked layered bisporphyrin structure of **3a,b**. Besides, UV-Vis spectra of **3** show a four-banded visible absorption characteristic of a free base porphyrin.



3a: Ar=PhH
3b: =$PhCH_3$

4 M=Fe
5 =Zn

Then, the central metal can be converted from cobalt to zinc[10] or iron[11] via **3b** in quantitative yields. A treatment of **3b** with $FeCl_2$ in THF under argon atmosphere at ice-water temperature gave a green complex **4b**, which could be purified only by recrystallization after dealing with saturated KCl aqueous solution. Treatment of **3b** in CH_2Cl_2 with saturated methanol solution of $Zn(AcO)_2$ under aerobic atmosphere at ambient temperature gave a green complex **5b**, after purification by chromatography on silica gel with CH_2Cl_2:acetone (10:1).

Each complex has a quite similar UV-Vis spectrum to those of *N*-substituted *meso*-tetraarylporphyrins which shows a Soret band at about 450 nm and a three-banded Q-band (so called Rhodo type).

The complex **4b** also shows a similar paramagnetic ^{1}H-NMR spectrum with a C_s symmetric pattern to that of **2b**, the assignment of which was made with the aid of line-width analysis and with reference to the spectra of **2** and N-Me(TPP)Fe^{II}Cl. The latter was reported by A. L. Balch et al.[10] The magnetic moment (μ=5.8) measured by Evans method in $CDCl_3$ at 25°C are close to the spin only value (μ=6.93) for two non-interacting d^6 high spin state Fe (S=2).[7] The ^{1}H-NMR chemical shifts-temperature plot of this complex obeyed the Curie law[7] as shown in Figure 3-9. It has been pointed out that iron(II) *N*-alkylporphyrin is less susceptible to oxygen than iron(II) porphyrin because the ligand field of a monoanionic *N*-substituted porphyrin is weaken and the *N*-alkyl group prevents oxygen from attacking iron. The d-orbital of iron nucleus is protected by a so rigid and great dimer structure that **4b** is extraordinarily stable in aerobic conditions. **5b** shows a diamagnetic ^{1}H-NMR spectrum with a C_s symmetric pattern and a remarkably temperature dependent line broadening as well as **3b**.

Table 3-5. The ^{1}H-NMR Spectral Data and the Yields of **9–10**

Compd.	Porphyrin Ligand				Other	Yield (%)
	β-Pyrrole	*o*–	*m*–	*p*–	Vinyl	
4a	41.5, 28.8	14.9, 11.8	13.2, 9.9	8.2		68
	0.6, -3.6	5.2, 2.7	9.3, 5.8	1.3		
4b	41.5, 27.9	14.7, 11.0	13.0, 9.7	6.0*		72
	0.6, -3.2	5.6, 2.3	9.2, 4.7	2.7*		
5a	8.92, 8.66				-5.87	80
	8.13, 6.83		8.0–5.2			
5b	8.92, 8.66			2.78*	-5.86	96
	8.16, 6.78		8.0–5.2	2.60*		

*) The signal intensity is 3H

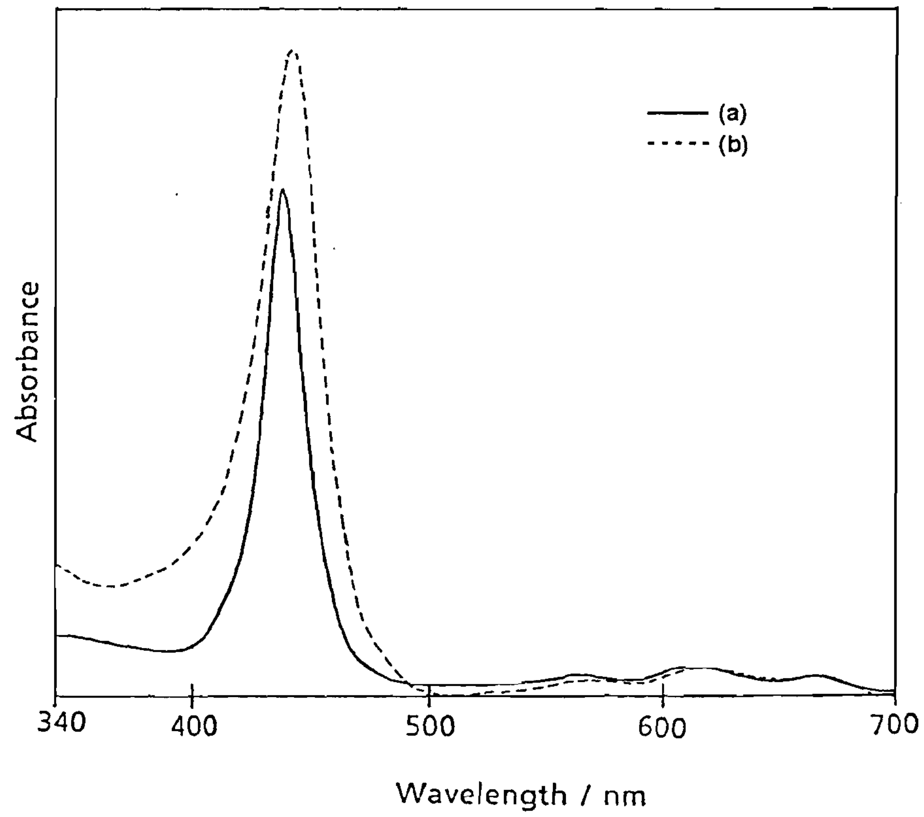


Figure 3-5. UV-Vis Spectra of (a) **4b** and (b) **5**

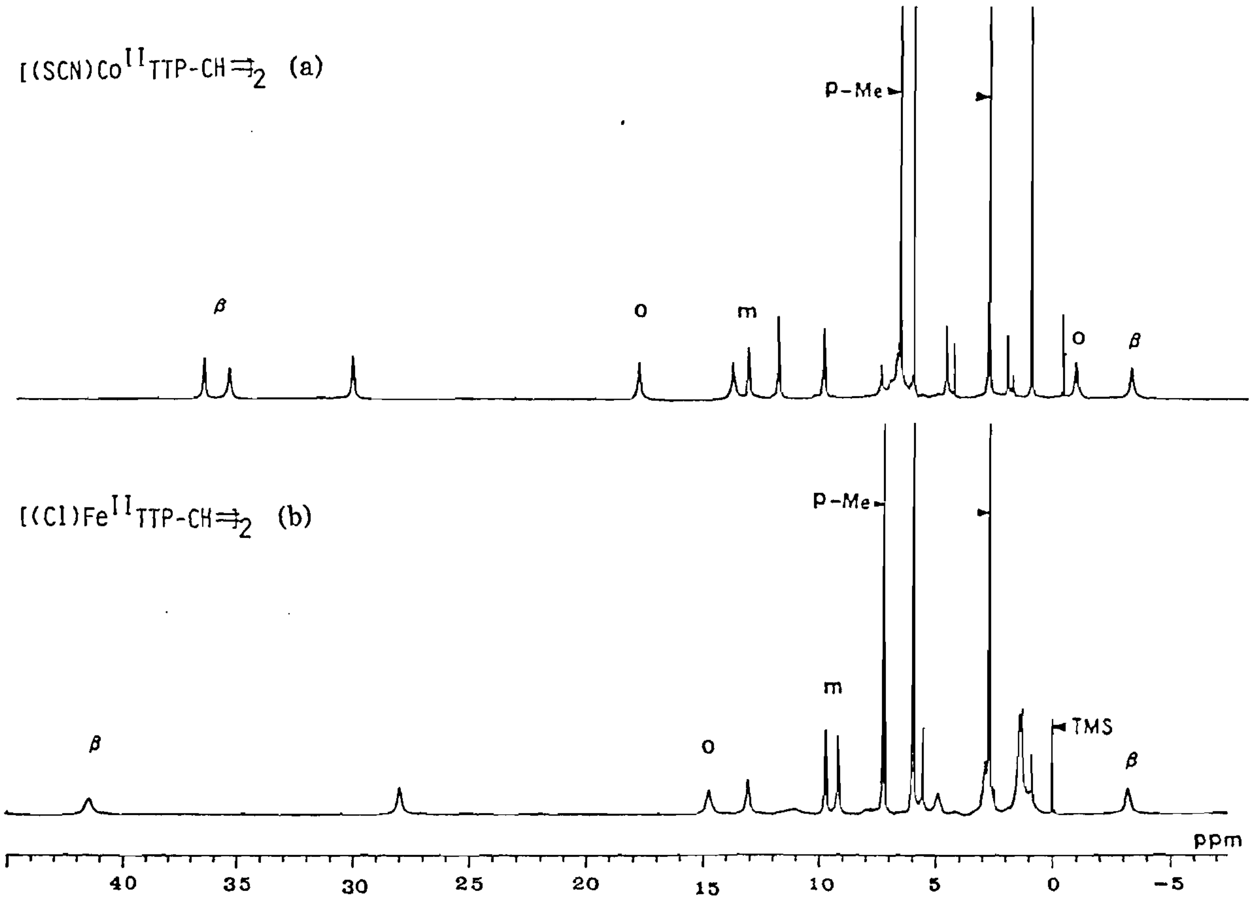


Figure 3-6. Paramagnetic ^{1}H-NMR Spectra of *N,N'*-Vinylene Bisporphyrin Complexes

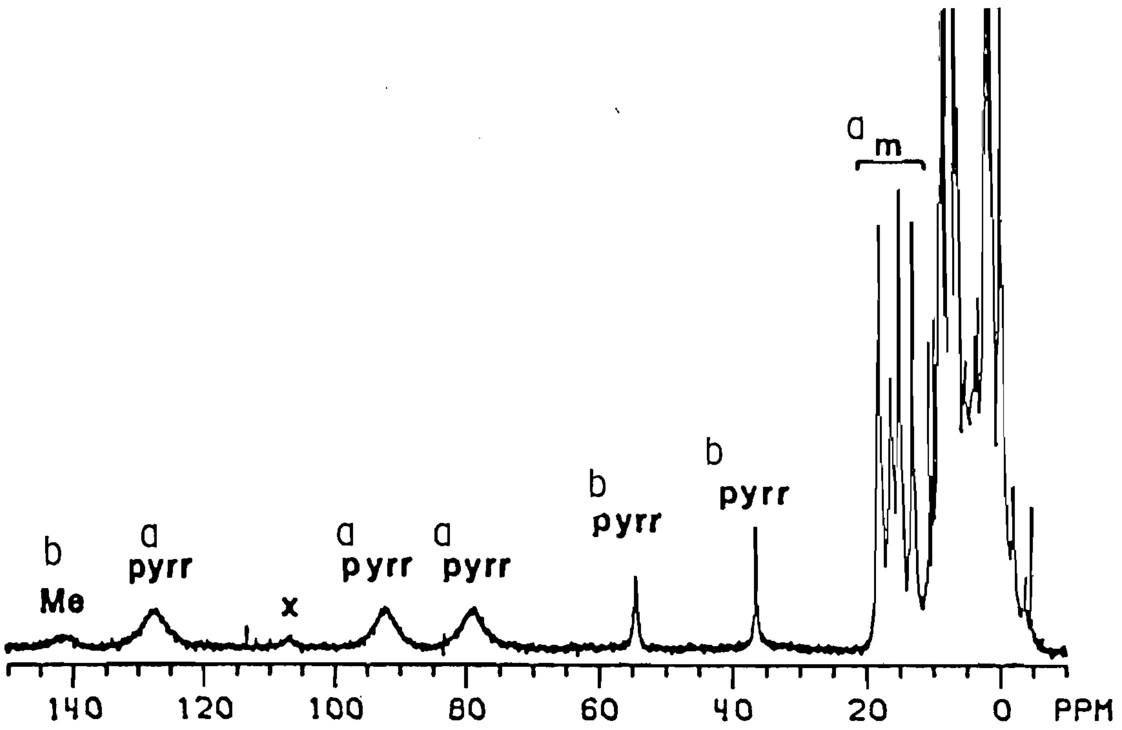


Figure 3-7. ^{1}H-NMR Spectra of (a) $[(\text{MeTPP})\text{Fe}^{\text{III}}\text{Cl}]^+$ and (b) $(\text{MeTPP})\text{Fe}^{\text{II}}\text{Cl}$ in $CDCl_3$ at −50°C Reported by A. L. Balch.

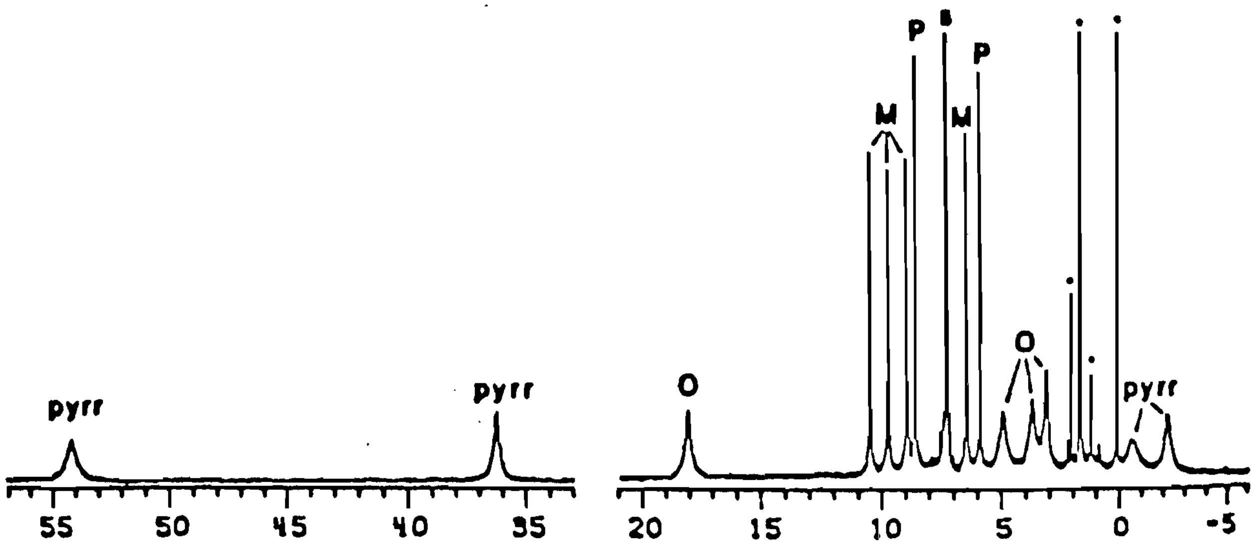


Figure 3-8. ^{1}H-NMR Spectra of $(\text{MeTPP})\text{Fe}^{\text{II}}\text{Cl}$ in $CDCl_3$ at −50°C Reported by A. L. Balch.

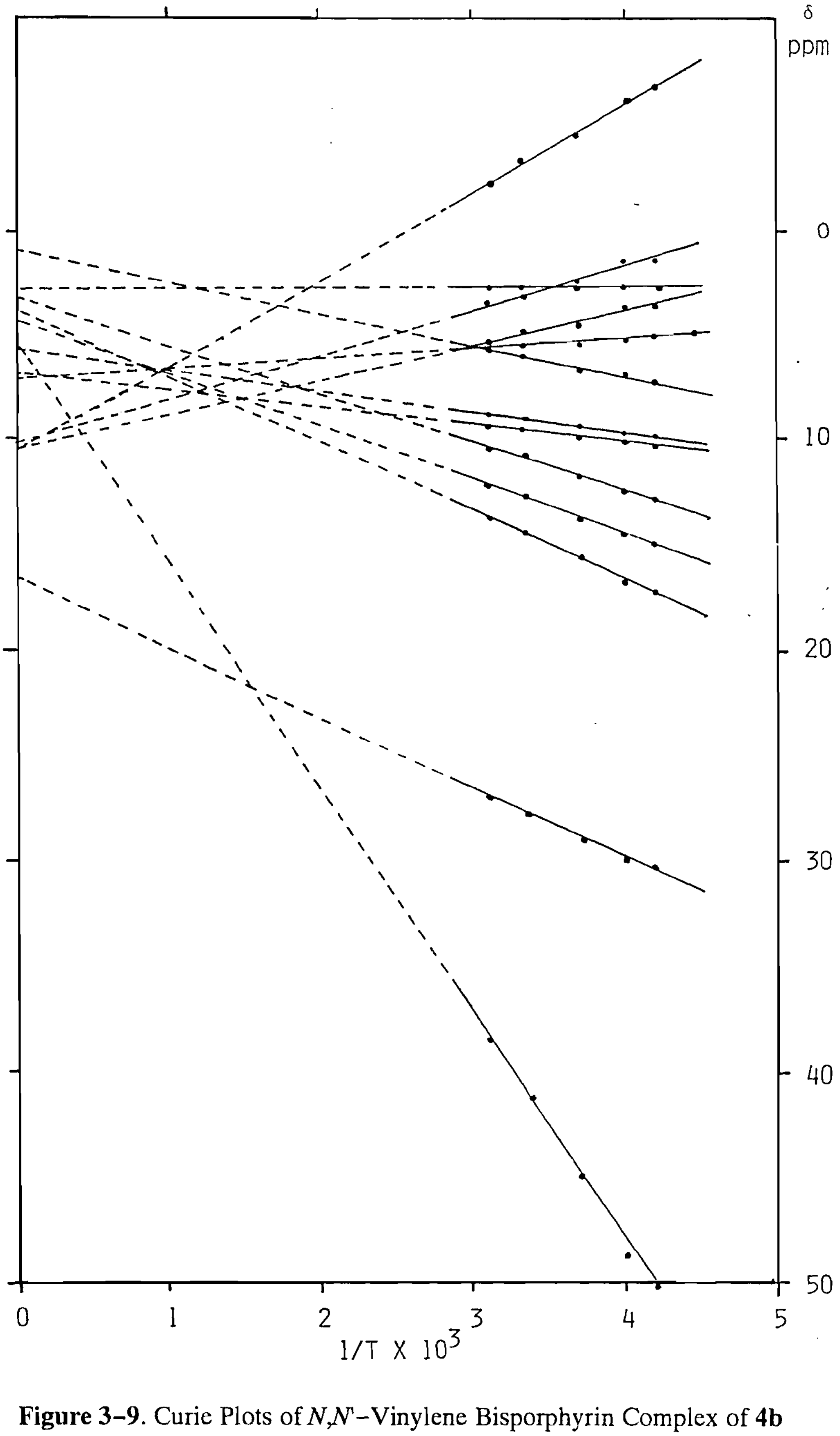
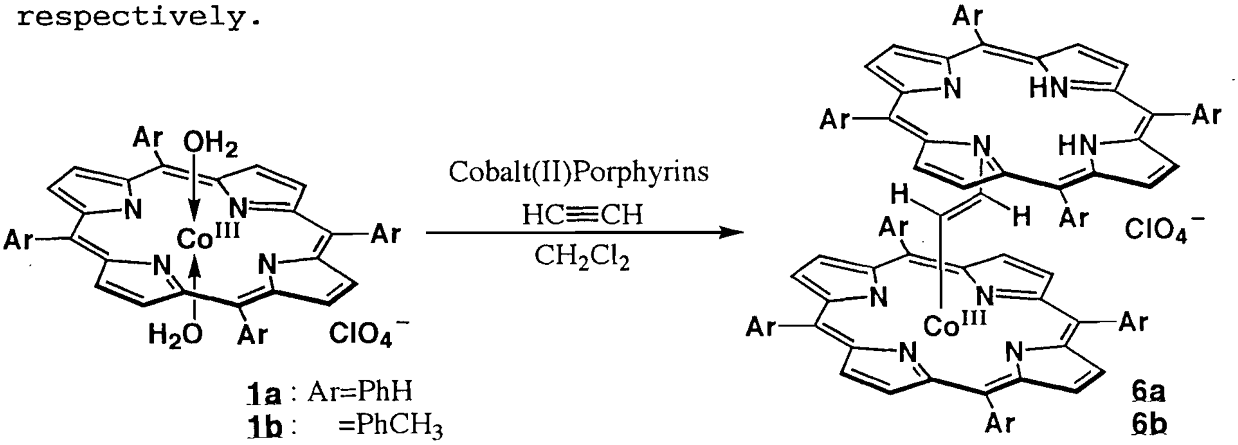


Figure 3–9. Curie Plots of *N*,*N'*–Vinylene Bisporphyrin Complex of **4b**

Synthesis and Properties of *Co,N*-Vinylene-linked Bisporphyrins

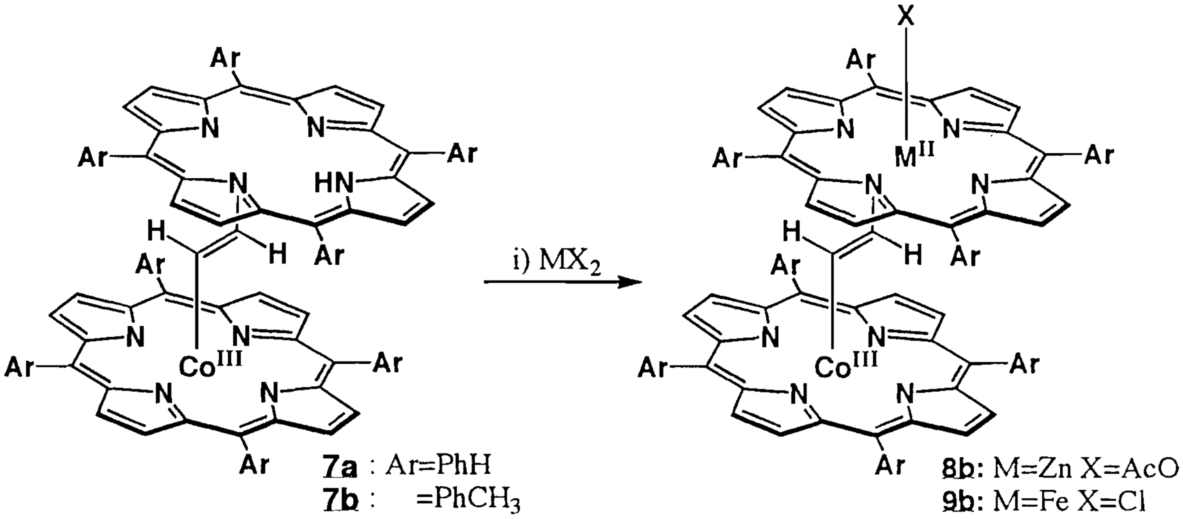
Introduction of acetylene gas into an equimolar mixture of **1a,b** and the corresponding cobalt(II) porphyrin in CH_2Cl_2 solution resulted in the formation of *Co,N'*-vinylene bisporphyrin $Co^{III}H_2ClO_4$ (**6a,b**) after chromatographic purification on silica gel with CH_2Cl_2-acetone (10:1). Although this *Co,N'*-vinylene linked bisporphyrin was isolated as a monometallic complex after chromatography, purification only by recrystallization from CH_2Cl_2-hexane allowed observation of the corresponding mixted valence biscobalt (II,III) complex as an initial product. The ^1H-NMR spectrum of this crude product showed four signals due to pyrrole β-positions at 47.8, 39.2, 36.6, and -8.3 ppm characteristic of cobalt(II) *N*-substituted porphyrins like **2**. But this complex is so unstable that the central metal is demetallated by the column chromatography on silica gel or aluminum oxide affording monocation or its free base (**7a,b**) in 37% and 37% yields, respectively.



1a : Ar=PhH
1b : =$PhCH_3$

6a
6b

Fe^{II} and Zn^{II} ions can be inserted into the porphyrin core of **7b** to give *Co,N'*-(CH=CH)$(TTP)_2Co^{III}Fe^{II}Cl$ (**8b**) and *Co,N'*-(CH=CH)$(TTP)_2Co^{III}Zn^{II}OAc$ (**9b**) under the same reaction conditions as in the case of **4b** and **5b**. Their UV-Vis spectra are similar and have a Soret band and a featureless Q-band as shown in Fig. 10. ^1H-NMR spectral data suggest that **8b** showing sharp signals is a paramagnetic complex with a d^6 high spin state and that **9b** is a diamagnetic complex with some broadened signals in comparison with the spectrum of **6b** owing to the more restricted rotation of *meso*-aryl groups caused by the incorporation of Zn^{-} ion.



7a : Ar=PhH
7b : =$PhCH_3$

8b: M=Zn X=AcO
9b: M=Fe X=Cl

We have recently found that acetylene reversibly reacts with two cationic cobalt(III) porphyrins via Co^{II}(porphyrin) acetylene π-complex intermediate which can be trapped by a bulky amine such as 2,6-lutidine to give σ-(β-2,6-lutidiniumvinyl)cobalt(III) porphyrin perchlorate (see Chapter II). Although bisporphyrins of OEP could not be obtained through the same procedures as those previously noted for **6a,b**, $OEPH_2$ and $TTPH_2$ cleanly reacted as a bulky amine toward the Co^{II}(porphyrin) acetylene π-complex intermediate analogously to 2,6-lutidine, giving rise to *Co,N'*-vinylene bisporphyrin $Co^{III}H_2ClO_4$ (**10a,b**) after chromatographic purification on silica gel with CH_2Cl_2:acetone (5:1) in 91% and 77% yields, respectively. The use of **1b** instead of **1c** gave **6b,c** in 36% and 38% yields, respectively.

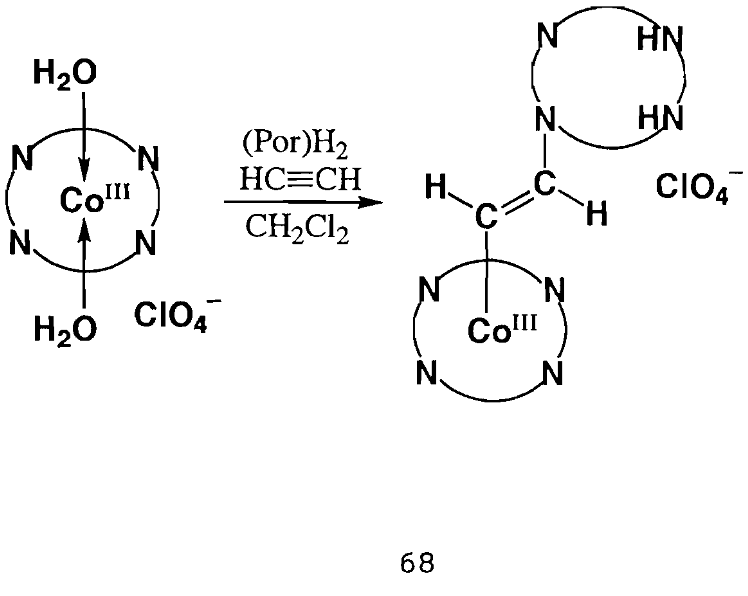


Table 3-6. λ_{max} Values of *Co,N*-Vinylene-Linked Bisporphyrins **6**-**7** and **10** (in CH_2Cl_2)

Compd.	λ_{max} Value(log ε)				
6a	413(5.40),	442(4.97),	537(4.16),	606(3.99),	661(4.11)
6b	415(5.44),	448(5.02),	532(4.38),	562(4.27),	666(4.34)
6c	396(5.51),	533(4.61)			
7a	409(5.38),	442(4.95),	543(4.23),	585(4.10),	660(3.97)
7b	413(5.01),	448(5.01),	535(4.25),	612(4.11),	664(4.20)
10a	383(5.30),	551(4.38)			
10b	390(5.06),	447(4.96),	551(4.17),	623(3.94),	659(397)

UV-Vis spectral data of *Co,N*'-vinylene bisporphyrin derivatives are shown in Table 3-6. Absorption bands characteristic of σ-alkyl cobalt(III) porphyrin and of *N*-substituted porphyrin appear separately in the spectra of these complexes. However, the absorption bands of both **6a,b,c** and **10a,b** are broadened in comparison to the corresponding absorptions of the monomeric component compounds. Such broadening is characteristic of cofacial bisporphyrin and is not unexpected in view of the proximity of the two porphyrin π-systems in **6a,b,c** and **10a,b**. The layered bisporphyrin structure with a *Co,N*'-vinylene linkage of **6b** was evidenced by the extremely up-field shifted pair of doublets due to the vinylene protons at -2.25 and -9.11 ppm (J_{trans}=12.0 Hz) at 0 °C and by the C_{4v} and C_s symmetric porphyrin resonances in 1:1 ratio like *Co,N*'-oxo linked bisporphyrin[4] in the ^1H-NMR spectrum. According to ^1H-^{13}C correlation NMR, the vinylic proton signal at -2.25 ppm is assigned to the α-position with respect to cobalt, whereas the vinylic proton signal at -9.11 ppm is assigned to the β-position. The extremely up-field shifted resonances are rationalized in terms of the theory that the region between two porphyrin planes is magnetically shielded by the doubled ring current effects of porphyrins. The *meso*-aryl signals of these complexes also showed remarkable temperature dependency caused by hindered rotation of *meso*-aryl groups as shown in Figure 3-11. A set of absorptions due to the *N*-substituted porphyrin are extremely broadened in comparison with a set of absorptions due to the σ-alkyl cobalt(III) porphyrin.

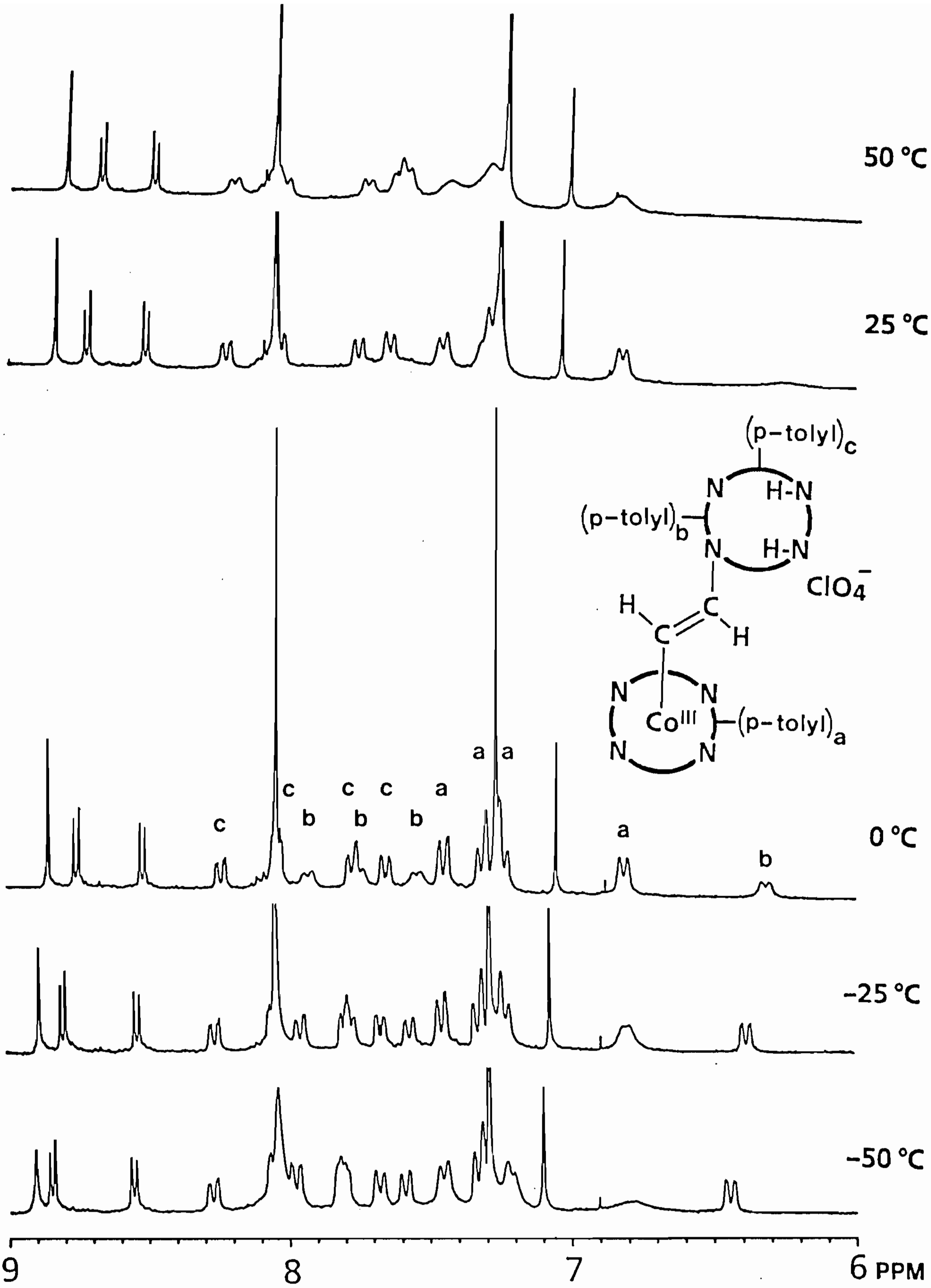


Figure 3-11. ^{1}H-NMR Spectrum of Aromatic Region of *Co,N'*-(HC=CH)(TTPCo^{III})(TTPH$_2$ClO$_4$)

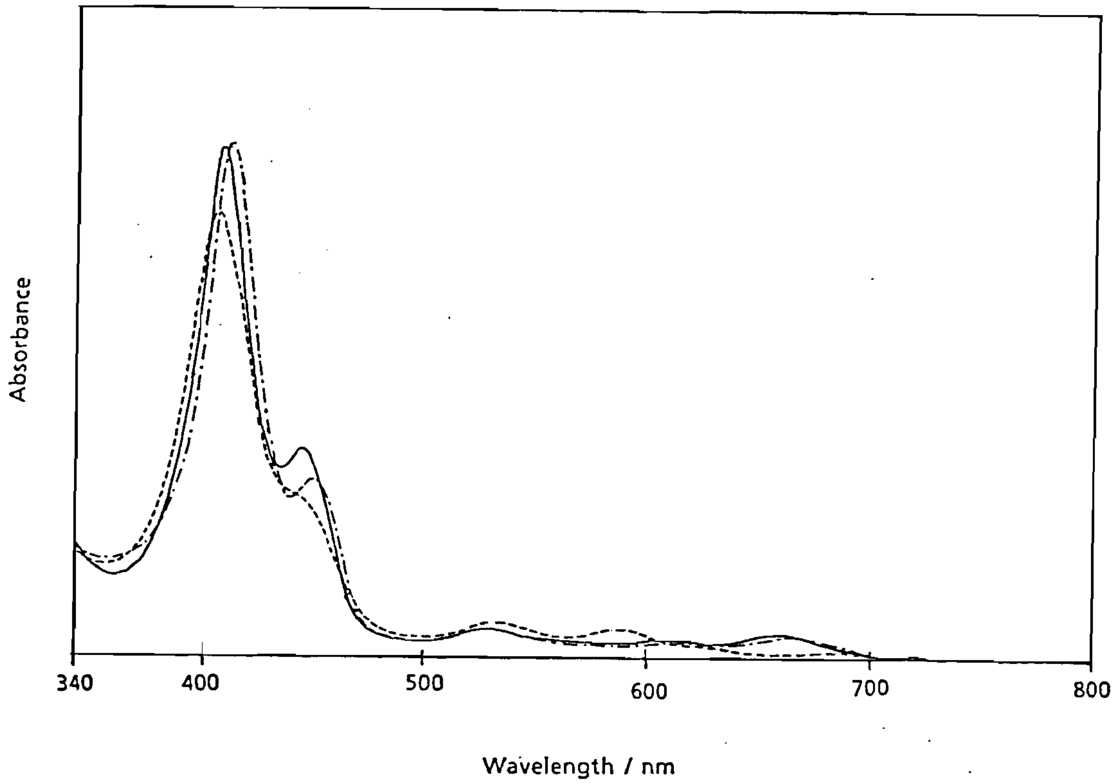


Figure 3-12. UV-Vis Spectra of (a) **11** and **12**

Cyclic voltammetric analysis of *Co,N'*-vinylene bisporphyrin derivatives shows that all complexes except **6b** have two reversible redox peaks at about $E_{1/2}$=1.1 V, 1.3 V for **6c** and 1.0 V, 1.3 V for **10a,b**. The first oxidation potentials of these complexes follow the order **6b**>**6c**>**10b**-**10a**. Therefore, it is dependent mainly on the cobalt porphyrin rather than on the *N*-substituted porphyrin. This suggests that the first oxidation occurs at the cobalt porphyrin site probably to give a Co^{III} π-cation radical.[11] The electron-donating groups at the periphery raise the HOMO energy level of OEP to facilitate oxidation of OEP in comparison with TTP. It has been known that *N*-(vinyl)porphyrinatocobalt(II) and -iron(II) complexes are interconvertible with σ-vinyl cobalt(III) and -iron(III) porphyrins by way of one electron redox process.[12] While reduction of **2** with $NaBH_4$ or $Na_2S_2O_4$ resulted in the loss of the vinylene linkage from cobalt to give the corresponding monomeric cobalt(II) porphyrin quantitatively, oxidation of **6a,b** with $Fe(ClO_4)_3$ (3 fold molar excess) for one hour in CH_2Cl_2 effected migration of the vinylene linkage to nitrogen with the bisporphyrin structure intact to give **3b** in 73% yield.

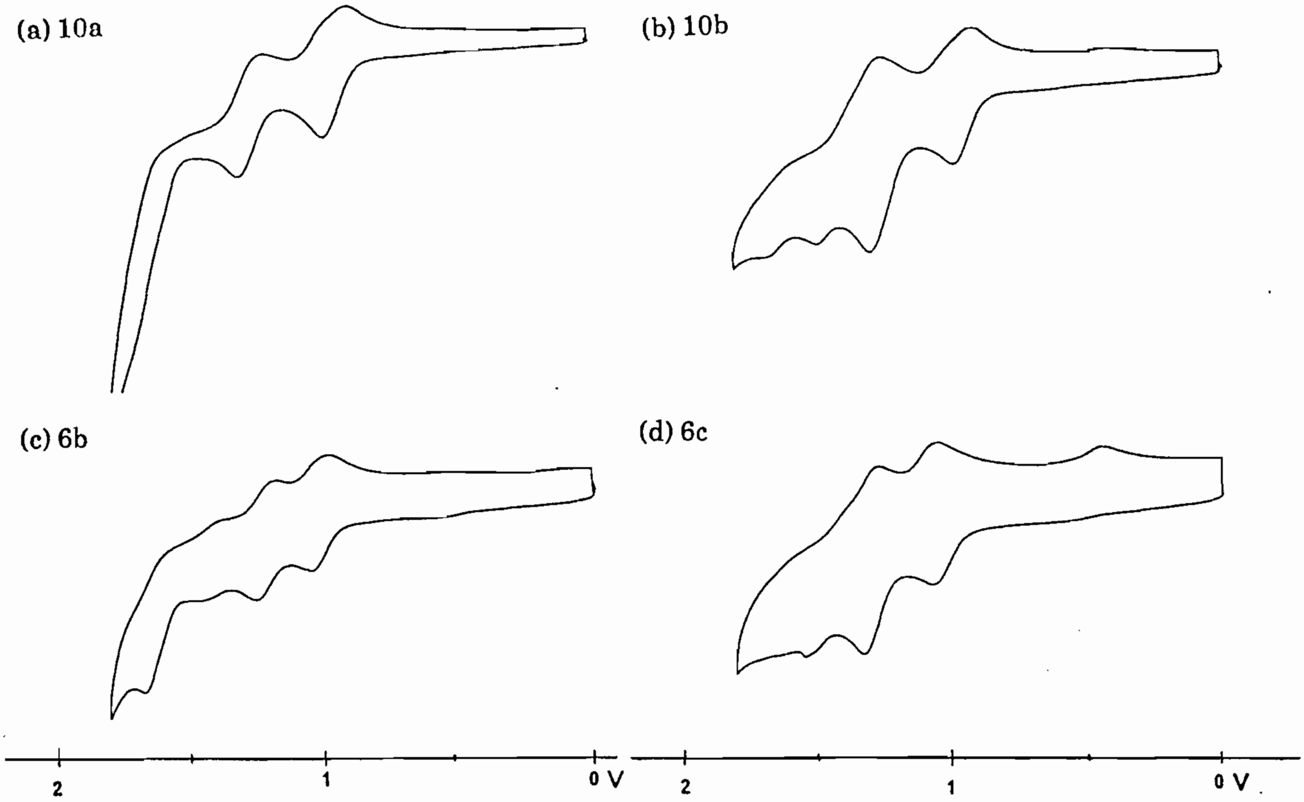
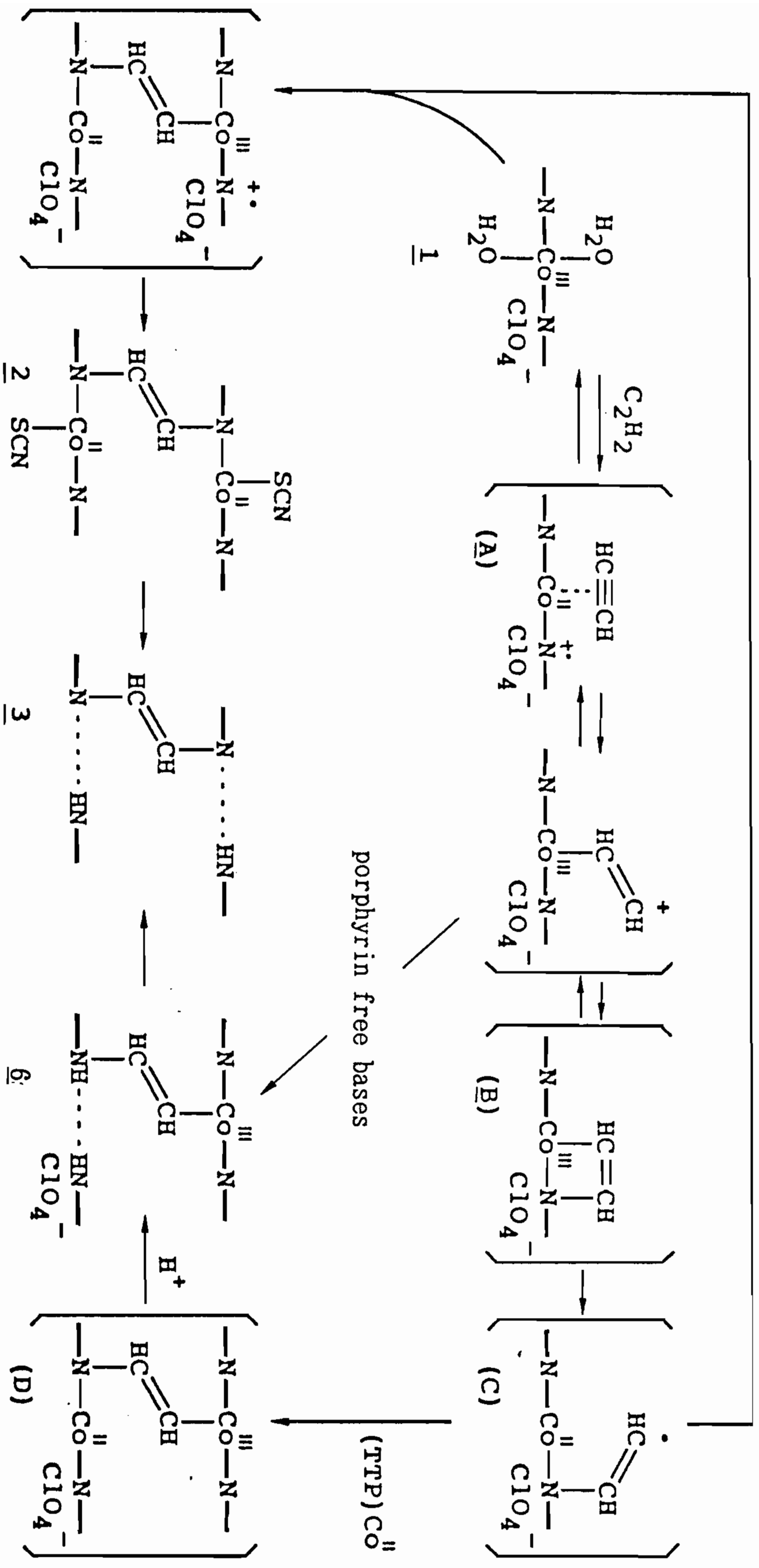


Figure 3–13. Cyclic Voltammograms in CH_2Cl_2, 0.1 M $(n\text{-}Bu_4N)ClO_4$, Measured against Ag/AgCl: (a) **10a**, (b) **10b**, (c) **6b**, (d) **6c**

The difference in the reaction behaviors of **1a** and **1c** toward acetylene is ascribable to the nature of the Co^{III}-carbon σ-bond of the *Co,N*-etheno bridged Co^{III} porphyrin intermediate (**B**). Since the electron-donating octaethyl substituents at the porphyrin periphery stabilize a high valent state of cobalt, heterolysis of the Co^{III}-carbon σ-bond leading to the dissociation to acetylene and **1c** would be favored. On the other hand, the Co^{III}-carbon σ-bond homolysis becomes the major reaction pathway in case of rather electron-withdrawing *meso*-tetraaryl substituents, resulting in the generation of cobalt(II) porphyrin *N*-vinyl radical (**C**) which is immediately trapped by cobalt(II) porphyrin to lead to **6a,b** and by **1** as a form of Co^{II} porphyrin π-cation radical in CH_2Cl_2 solution to lead to **2b**.



Scheme 3–1. Reaction Mechanism

Table 3-7. The List of Elemental Analysis Data

Compd.	Formula		H	C	N
2a	$C_{92}H_{58}N_{10}S_2Co_2$	Found	3.52	73.55	9.22
		(Calc.)	(3.94)	(74.38)	(9.43)
2b	$C_{100}H_{74}N_{10}S_2Co_2$	Found	4.40	74.09	8.60
		(Calc.)	(4.67)	(75.17)	(8.77)
2b'	$C_{98}H_{74}N_8Cl_2Co_2$	Found	4.50	73.97	7.03
		(Calc.)	(4.80)	(75.82)	(7.22)
3a	$C_{90}H_{60}N_8$	Found	4.82	86.24	8.94
		(Calc.)	(4.39)	(81.60)	(8.05)
3b	$C_{98}H_{76}N_8$	Found	5.20	82.58	7.73
		(Calc.)	(5.61)	(86.19)	(8.20)
		(Calc.)	(4.08)	(75.38)	(7.81)
4b	$C_{98}H_{74}N_8Cl_2Fe_2$	Found	4.91	75.15	7.16
		(Calc.)	(4.82)	(76.12)	(7.25)
5b	$C_{98}H_{74}N_8Cl_2Zn_2$	Found	4.78	74.10	6.40
		(Calc.)	(4.76)	(75.19)	(7.16)
6a	$C_{90}H_{60}N_8O_4ClCo$	Found	4.00	75.32	7.58
		(Calc.)	(4.28)	(76.56)	(7.94)
6b	$C_{98}H_{76}N_8O_4ClCo$	Found	5.11	75.49	7.19
		(Calc.)	(5.03)	(77.23)	(7.35)
7a	$C_{90}H_{59}N_8Co$	Found	4.60	81.09	6.47
		(Calc.)	(4.53)	(82.43)	(8.54)
7b	$C_{98}H_{75}N_8Co$	Found	3.86	73.23	9.15
		(Calc.)	(5.31)	(82.68)	(7.87)
10a	$C_{74}H_{92}N_8O_4CoCl$	Found	7.28	70.79	8.84
		(Calc.)	(7.40)	(70.99)	(8.95)
10b	$C_{86}H_{84}N_8O_4CoCl$	Found	5.18	72.81	7.29
		(Calc.)	(6.10)	(74.42)	(8.07)

Experimental Section

General Comments. ^{1}H-, and ^{13}C-NMR spectra were recorded in deuteriochloroform by using a JEOL GX-270 spectrometer (270MHz, 67.8MHz), and ^{1}H-chemical shifts are referenced to tetramethylsilane, and ^{13}C-chemical shifts are measured relative to the signal of solvent ($\delta(CDCl_3)$ 77.05ppm). Coupling constants of pyrrolic and aromatic protons are in a normal range of about 5 and 8 Hz, respectively, and will not be specified. UV-Vis spectra were taken in CH_2Cl_2 solution on a Shimadzu UV-240 or a Shimadzu UV-245Fs spectrometer. IR spectra measurements were made in a KBr disk with a Shimadzu IR-420 spectrometer. Cyclic Voltammetric analysis was made with a Yanaco VMA-10. Measurements were carried out on a glassy carbon electrode with a sweep rate of 50 mV/s and in the range of 0-2.0 V by using Ag/AgCl couple as a reference electrode and tetra-n-butylammonium perchlorate as electrolyte. Elemental Analyses were performed on a Yanaco CHN MT2 recorder using acetanilide as a standard compound. Wakogel C-300 was used for silica gel column chromatography. Merck Aluminum oxide 90 was used for alumina column chromatography. Most reactions were monitored by using a Kieselgel 60F254 silica gel TLC plate. TPP(d_8)H_2 was prepared by literature procedures.[13]

Formation of *N,N'*-Vinylene Bisporphyrins

***N,N'*-(CH=CH)(TPPCo^{II}SCN)$_2$ 2a** (TPP)Co^{III}(H_2O)$_2$ClO$_4$ (**1a**) (ca. 50 mg) was dissolved in CH_2Cl_2 (ca. 30 ml) at ambient temperature under aerobic atmosphere. Bubbling acetylene gas changed the color of the solution from red to green. After stirring for half an hour, the reaction mixture was dealt with saturated NaSCN aqueous solution (ca. 30 ml) for more half an hour. The CH_2Cl_2 layer was washed with water twice in a separatory funnel, and dried over Na_2SO_4. After removal of CH_2Cl_2, the residue was chromatographed on silica gel with CH_2Cl_2 in order to purify products. The first green band collected was slightly contaminated with the second red band. Recrystallization from CH_2Cl_2-methanol removed cationic cobalt(III) complexes and gave **1a** as purple crystals in 48% yield: ^1H-NMR δ($CDCl_3$) -3.4, 33.8, 40.2, 41.8 (singletx4, 4Hx4, β-pyrrole), -0.6, 9.5, 16.3, 20.8 (singletx4, 4Hx4, *meso-o*-Ph), 5.8, 11.8, 13.9, 15.4 (singletx4, 4Hx4, *meso-m*-Ph), 8.7, 9.5 (singletx2, 4Hx2, *meso-p*-Ph); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 442(5.33), 567(4.07), 618(4.22), 661(4.00); Anal. Calcd for $C_{92}H_{58}N_{10}S_2Co_2H_2O$: C,73.49; H,4.02; N,9.32. Found. C,73.55; H,3.52; N,9.22.

***N,N*'-(CH=CH)(TTPCo^{II}SCN)$_2$ 2b**; The reaction was performed by using (TTP)Co^{III}(H_2O)$_2$ClO$_4$ (**1b**). According to the above procedure, **2b** was obtained in 60% yield: ^1H-NMR δ($CDCl_3$) -3.3, 34.3, 40.3, 41.5 (singletx4, 4Hx4, β-pyrrole), -0.6, 8.8, 15.9, 20.4 (singletx4, 4Hx4, *meso-o*-Ph), 5.6, 11.6, 13.7, 15.2 (singletx4, 4Hx4, *meso-m*-Ph), 3.6, 7.9 (singletx2, 12Hx2, *meso-p*-Me); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 445(5.29), 570(4.06), 621(4.21), 666(4.03); Anal. Calcd for $C_{100}H_{74}N_{10}S_2Co_2H_2O$: C,74.09; H,4.74; N,8.67. Found. C,74.09; H,4.40; N,8.60.

***N,N*'-(CH=CH)(TTPCo^{II}Cl)$_2$ 2b'**; The reaction was performed by using (TTP)Co^{III}(H_2O)$_2$ClO$_4$ (**1b**) and worked-up according to the above procedure except that NaSCN was replaced with NaCl. Chromatography on silica gel with CH_2Cl_2-acetone (10:1) and recrystallization from CH_2Cl_2-methanol gave **2b'** as purple crystals in 56% yield: ^1H-NMR δ($CDCl_3$) -8.4, 36.8, 39.5, 48.1 (singletx4, 4Hx4, β-pyrrole), 1.1, 5.4, 18.1, 20.1 (singletx4, 4Hx4, *meso-o*-Ph), 6.1, 11.7, 14.0, 14.3 (singletx2, 12Hx2, *meso-m*-Ph), 3.8, 7.7 (singletx4, 12Hx4, *meso-p*-Me), -178 (singlet, 1Hx2, vinyl-H) ; UV-Vis(CH_2Cl_2) λ_{max} (log ε) 442(5.27), 544(4.12), 618(4.13), 665(3.95); Anal. Calcd for $C_{98}H_{74}N_8Cl_2Co_2$: C,74.10; H,4.95; N,7.05. Found. C,73.97; H,4.50; N,7.03.

***N,N*'-(CH=CH)(TPPH)$_2$ 3a**; *N,N*'-(CH=CH)(TPPCo^{II}SCN)$_2$ **2a** (ca.30 mg) in CH_2Cl_2 (ca. 20 ml) was treated with trifluoroacetic acid (ca. 1 ml). After stirring for 15 min at ambient temperature under aerobic atmosphere the solution was neutralized (aqueous NH_3) to precipitate microcrystals which was washed with water, dried over Na_2SO_4, and recrystallized from CH_2Cl_2-hexanes. The yield is 79%.: ^{1}H-NMR δ($CDCl_3$) 6.12, 8.86, 7.96, 8.27 (singletx2, doubletx2, 4Hx4, β-pyrrole), -5.32 (singlet, 1Hx2, bridge vinyl-H), -3.1 (broad singlet, 1Hx2, NH), 5.4~8.5 (multiplet, 40H, *meso*-Ph); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 415(5.39), 531(4.15), 571(4.17), 623(3.80), 683(3.82); Anal. Calcd for $C_{90}H_{60}N_8$: C,86.24; H,4.82; N,8.94. Found. C,81.60; H,4.39; N,8.05.

***N,N'*-(CH=CH)(TTPH)$_2$ 3b**; The reaction was performed by using *N,N'*-(CH=CH)(TTPCo^{II}SCN)$_2$ **2b** instead of **2a** in the above procedure. According to the above work-up procedure, **3b** was obtained in 87% yield: ^{1}H-NMR δ($CDCl_3$) 6.08, 8.86, 7.96, 8.26 (singletx2,doubletx2, 4Hx4, β-pyrrole), -5.33 (singlet, 1Hx2, bridge vinyl-H), 2.57, 2.79 (singletx2, 12Hx2, *meso-p*-Me), -3.1 (broad singlet, 1Hx2, NH), 5.4~8.3 (multiplet, 32H, *meso*-Ph); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 425(5.52), 532(4.04), 576(4.26), 625(4.10), 680(4.10); Anal. Calcd for $C_{98}H_{76}N_8$: C,87.73; H,5.71; N,8.35. Found. C,82.58; H,5.20; N,7.73.

***N,N'*-(CH=CH)(TPPFe^{II}Cl)$_2$ 4a**; $FeCl_3$ (ca. 5 eq.) and excess iron powder were placed in a two-necked flask fitted with a sealed rubber septum and a reflux condenser which was joined to a vacuum pump and an argon line. When the atmosphere was replaced with argon, distilled and aerated dry THF was added with a syringe by way of a rubber septum. The reaction mixture was refluxed under argon for several hours and then cooled in an ice bath. THF solution of *N,N'*-(CH=CH)(TPPH)$_2$ **3a** was added to this mixture with a syringe via a rubber septum. The solution rapidly turned green, and then a stoichiometric amount of a noncoordinating base, tetramethylpiperidine or 2,6-lutidine, was added. After stirring an hour at 0 °C, the reaction mixture was filtered and evaporated to dryness. The residue was dissolved in CH_2Cl_2 and treated with saturated KCl aqueous solution for half an hour. The CH_2Cl_2 layer was dried over Na_2SO_4. Recrystallization from

CH_2Cl_2-hexanes gave **4a** in 68% yield: ^{1}H-NMR δ($CDCl_3$) -3.6, 28.8, 41.5, 0.6 (singletx4, 2Hx4, β-pyrrole), 2.7, 11.8, 14.9, 5.2 (singletx4, 4Hx4, *meso-o*-Ph), 9.3, 5.7, 9.9, 13.2 (singletx4, 4Hx4, *meso-m*-Ph), 1.3, 8.2 (singletx2, 12Hx2, *meso-p*-Me); UV-Vis(CH_2Cl_2) λ_{max} (log ε); Anal. Calcd for $C_{90}H_{58}N_8Cl_2Fe_2$: C,75.38; H,4.08; N,7.81. Found.

***N,N'*-(CH=CH)(TTPFe^{II}Cl)$_2$ 4b**; The reaction was performed by using *N,N'*-(CH=CH)(TTPH)$_2$ **3b** instead of **3a** in the above procedure. According to the above work-up procedure **4b** in 72% yield: ^{1}H-NMR δ($CDCl_3$) -3.2, 27.9, 41.4 (singletx3, 2Hx3, β-pyrrole one signal could not be detected.), 4.7, 11.0, 13.0, 14.7 (singletx4, 4Hx4, *meso-o*-Ph), 2.3, 5.6, 9.2, 9.7 (singletx4, 4Hx4, *meso-m*-Ph), 2.7, 6.0 (singletx2, 12Hx2, *meso-p*-Me); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 442(5.42), 570(4.19), 619(4.29), 668(4.21); Anal. Calcd for $C_{98}H_{76}N_8Cl_2Fe_2H_2O$: C,75.24; H,4.92; N,7.16. Found. C,75.15; H,4.92; N,7.16.

***N,N'*-(CH=CH)(TPPZn^{II}Cl)$_2$ 5a**; *N,N'*-(CH=CH)(TPPH)$_2$ 3a was dissolved in CH_2Cl_2 (10 ml) under aerobic conditions, and then was added saturated $Zn(AcO)_2$ methanol solution (ca. 5 ml). The solution rapidly turned green and then a stoichiometric amount of a noncoordinating base, tetramethylpiperidine or 2,6-lutidine, was added. After stirring half an hour at room temperature, the reaction mixture was evaporated under vacuum. The residue was dissolved in CH_2Cl_2 and treated with saturated KCl aqueous solution for half an hour. The CH_2Cl_2 layer was dried over Na_2SO_4. After removal of CH_2Cl_2, the residue was chromatographed on silica gel with CH_2Cl_2-acetone (10:1) to purify the desired product which could be collected as a green band. Recrystallization from CH_2Cl_2-hexane afforded 5b in 80% yield: ^{1}H-NMR δ($CDCl_3$) 6.83, 9.92, 8.13, 8.66 (singletx2,doubletx2 4Hx4, β-pyrrole), -5.87 (singlet, 1Hx2, bridge vinyl-H), 3.5~8.0 (multiplet, 16H, *meso*-Ph); UV-Vis(CH_2Cl_2) λ_{max} (log ε) Anal. Calcd for $C_{90}H_{58}N_8Cl_2Zn_2$: C,74.39; H,4.02; N,7.71.

***N,N*'-(CH=CH)(TTPZn^{II}Cl)$_2$ 5b**; *N,N*'-(CH=CH)(TTPH)$_2$ **3b** was dissolved in CH_2Cl_2 (10 ml) under aerobic conditions, and then was added saturated Zn(AcO)$_2$ methanol solution (ca. 5 ml). The solution rapidly turned green and then a stoichiometric amount of a noncoordinating base, tetramethylpiperidine or 2,6-lutidine, was added. After stirring half an hour at room temperature, the reaction mixture was evaporated under vacuum. The residue was dissolved in CH_2Cl_2 and treated with saturated KCl aqueous solution for half an hour. The CH_2Cl_2 layer was dried over Na_2SO_4. After removal of CH_2Cl_2, the residue was chromatographed on silica gel with CH_2Cl_2:acetone (10:1) to purify the desired product which could be collected as a green band. Recrystallization from CH_2Cl_2-hexane afforded **5b** in 96% yield: ^{1}H-NMR δ($CDCl_3$) 6.78, 9.92, 8.16, 8.66 (singletx2,doubletx2 4Hx4, β-pyrrole), -5.86 (singlet, 1Hx2, bridge vinyl-H)), 2.60, 2.78 (singletx2, 12Hx2, *meso*-*p*-Me), 5.2~8.0 (multiplet, 16H, *meso*-Ph); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 438(5.65), 565(4.12), 615(4.35), 664(4.21); Anal. Calcd for $C_{98}H_{76}N_8Cl_2Zn_2$: C,75.19; H,4.76; N,7.16. Found. C,74.10; H,4.78; N,6.40.

Formation of *Co,N*'-Vinylene Bisporphyrins

***Co,N*'-(CH=CH)(TPPCo^{III})(TPPH$_2$)ClO$_4$ 6a**; An equimolar mixture of (TPP)Co^{III}(H_2O)$_2$ClO$_4$ (**1a**) and TPPCo^{II} was completely dissolved in CH_2Cl_2 (ca. 200 ml). When acetylene gas was allowed to bubble at least for half an hour at room temperature under aerobic conditions, the color of the reaction mixture changed from red to brown-green. After the solution was concentrated and filtered, the filtrate was chromatographed on silica gel with CH_2Cl_2-acetone (10:1) in order to purify the desired product which could be collected as the first brown-green band. Recrystallization from CH_2Cl_2-hexane afforded **6a** in 40% yield: ^{1}H-NMR δ($CDCl_3$) 8.16 (singlet, 8H, β-pyrrole of *Co*-porphyrin), 7.06, 8.80, 8.64, 8.47 (singletx2, doubletx2, 2Hx4, β-pyrrole of *N*-porphyrin), -8.97, -2.30 (doubletx2, 1Hx2, bridge vinyl-H, J_{trans}=11.5Hz), 6.3~8.4 (multiplet, 40Hx4, *meso*-Ph); UV-Vis(CH_2Cl_2) λ_{max} (log ε)

413(5.40), 442(4.97), 537(4.16), 606(3.99), 661(4.11); Anal. Calcd for $C_{90}H_{60}N_8O_4ClCo$: C,76.61; H,4.21; N,7.94. Found. C,75.32; H,4.00; N,7.85.

***Co,N'*-(CH=CH)(TTPCo^{III})(TTPH$_2$)ClO$_4$ 6b**; The reaction was performed by using an equimolar mixture of (TTP)Co^{III}(H$_2$O)$_2$ClO$_4$ (**1b**) and TTPCo^{II} and worked-up according to the above procedure. The yield is 37%: ^{1}H-NMR δ(CDCl$_3$, 0°C) 8.05 (singlet, 8H, ь-pyrrole of *Co*-porphyrin), 7.06, 8.86, 8.51, 8.76 (singletx2, doubletx2, 2Hx4, β-pyrrole), 6.32, 7.53, 7.65, 7.77 (broad doubletx2, doublet of doubletsx2 2Hx4, *meso-o*-Ph of *N*-porphyrin), 6.82, 7.24 (doubletx2, 4Hx2, *meso-o*-Ph of *Co*-porphyrin), 7.75, 7.93, 8.04, 8.24 (broad doubletx2, doublet of doubletsx2 2Hx4, *meso-m*-Ph of *N*-porphyrin), 7.32, 7.45 (doubletx2, doublet of doubletsx2 2Hx4, *meso-m*-Ph of *Co*-porphyrin), 2.82, 2.83 (singlet, 12H, *meso-p*-Ph of *N*-porphyrin), 2.73 (singletx2, 6Hx4, *meso-p*-Ph of *N*-porphyrin), -9.11, -2.25 (doubletx2, 1Hx2, bridge vinyl-H, J_{trans}=12.0); UV-Vis(CH$_2$Cl$_2$ λ_{max} (log ε) 415(5.44), 448(5.02), 532(4.38), 562(4.27), 666(4.34); Anal. Calcd for $C_{98}H_{76}N_8O_4ClCo_2H_2O$: C,78.49; H,4.70; N,7.18. Found. C,75.49; H,5.11; N,7.19.

***Co,N'*-(CH=CH)(TPPCo^{III})(TPPH) 7a**; The reaction was performed by using an equimolar mixture of (TPP)Co^{III}(H$_2$O)$_2$ClO$_4$ (1a) and TPPCo^{II} and worked-up according to the above procedure. Chromatography on aluminum oxide with CH$_2$Cl$_2$:acetone (10:1) afforded the desired product as the first brown-green band. Recrystallization from CH$_2$Cl$_2$-hexane afforded **7a** in 22% yield: ^{1}H-NMR δ(CDCl$_3$) 8.10 (singlet, 8H, β-pyrrole of *Co*-porphyrin), 6.35, 9.77, 7.91, 8.05 (singletx2, doubletx2, 2Hx4, β-pyrrole of *N*-porphyrin), -7.88, -2.67 (doubletx2, 1Hx2, bridge vinyl-H, J_{trans}=11.9 Hz), 6.5-8.1 (multiplet, 40Hx4, *meso*-Ph); UV-Vis(CH$_2$Cl$_2$) λ_{max} (log ε) 409(5.38), 442(4.95), 534(4.23), 585(4.10), 627, 660(3.97); Anal. Calcd for $C_{90}H_{59}N_8Co$: C,82.36; H,4.53; N,8.54. Found. C,81.09; H,4.60; N,6.47.

***Co,N'*-(CH=CH)(TTPCo^{III})(TPPH) 7b**; The reaction was performed by using an equimolar mixture of (TPP)Co^{III}(H_2O)$_2$$ClO_4$ (**1b**) and TTPCo^{II} and worked-up according to the above procedure. The yield is 37%: ^{1}H-NMR δ($CDCl_3$, -25°C) 8.07 (singlet, 8H, β-pyrrole of *Co*-porphyrin), 6.43, 8.80, 7.88, 8.08 (singletx2, doubletx2, 2Hx4, β-pyrrole), 6.4~8.3 (multiplet, 40Hx4, *meso*-Ph), 2.76, 2.77 (singletx2, 6Hx2, *meso-p*-Me of *N*-porphyrin), 2.70 (singlet, 12H, *meso-p*-Me of *Co*-porphyrin), -10.34, -4.79 (doubletx2, 1Hx2, bridge vinyl-H, J_{trans}=11.7Hz); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 413(5.42), 448(5.01), 535(4.25), 612(4.11), 625, 664(4.20); Anal. Calcd for $C_{98}H_{75}N_8Co$: C,78.59; H,4.21; N,9.75. Found. C,73.23; H,3.86; N,9.15.

***Co,N'*-(CH=CH)(TPPCo^{III})(TPPCo^{II})ClO_4** ; The reaction was performed by using an equimolar mixture of (TPP)Co^{III}(H_2O)$_2$$ClO_4$ (**1a**) and TPPCo^{II}. Acetylene gas was allowed to bubble for half an hour at room temperature under aerobic conditions. Then, the color of the reaction mixture changed from red to brown-green. The solution was filtered in order to remove excess TPPCo^{II} and repeatedly recrystallized from solution of CH_2Cl_2-hexane (three times). The yield is 56%: ^{1}H-NMR δ($CDCl_3$) -8.3, 36.6, 39.2 47.8(singletx4, 4Hx4, β-pyrrole); UV-Vis(CH_2Cl_2) λ_{max} 423, 548, 623, 658.

***Co,N'*-(CH=CH)(TTPCo^{III})(TTPFe^{II})Cl 8b**; $FeCl_3$ (ca. 5 eq.) and excess iron powder were placed in a two-necked flask fitted with a sealed rubber septum and a reflux condenser which was joined to a vacuum pump and an argon line. When the atmosphere was replaced with argon, distilled and aerated dry THF was added with a syringe by way of a rubber septum. The reaction mixture was refluxed under argon for several hours and then cooled in an ice bath. THF solution of *Co,N'*-(CH=CH)(TTP)$_2$Co^{III}H **7b** was added with a syringe via a rubber septum. The solution rapidly turned green. After stirring an hour at 0 °C, and then a stoichiometric amount of a noncoordinating base, tetramethylpiperidine or 2,6-lutidine, was added. The reaction mixture was filtered and repeatedly recrystallized from solution of CH_2Cl_2-hexane (three times) to give **8b** in 100% yield.: ^{1}H-NMR No signal peaks could be detected over the range of 100 ppm.; UV-Vis(CH_2Cl_2) λ_{max} 408, 450(sh), 528, 623, 668

***Co*,*N*'-(CH=CH)(TTPCo^{III})(TTPZn^{II})OAc 9b**; **6b** dissolved in CH_2Cl_2 under aerobic conditions, and then was added saturated $Zn(AcO)_2$ methanol solution. The solution rapidly turned green. After stirring half an hour at room temperature, the reaction mixture was filtered and repeatedly recrystallized from solution of CH_2Cl_2-hexane (three times) to give **9b** in 100% yield.: ^{1}H-NMR δ($CDCl_3$) 8.05 (singlet, 8H, β-pyrrole of *Co*-porphyrin), 6.58, 8.97, 8.24, 8.46 (singletx2, doubletx2, 2Hx4, β-pyrrole), 6.2~8.2 (multiplet, 40Hx4, *meso*-Ph), 2.73, 2.76 (singletx2, 6Hx2, *meso*-*p*-Me of *N*-porphyrin), 2.67 (singlet, 12H, *meso*-*p*-Me of *N*-porphyrin), -8.58, -2.60 (doubletx2, 1Hx2, bridge vinyl-H, J_{trans}=12.2Hz); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 410, 455(sh), 532, 630, 668

***Co*,*N*'-(CH=CH)(OEPCo^{III})(OEPH$_2$)ClO$_4$ 10a**; (OEP)Co^{III}(H_2O)$_2$ClO$_4$ (**1a**) and OEPH$_2$ (ca. 1.5 eq.) were placed in a three-necked flask fitted with a sealed rubber septum, a gas inert port for introducing acetylene gas, and a three-way stop-cock which was joined to a vacuum pump and a balloon. When the atmosphere was replaced with acetylene gas, the CH_2Cl_2 at 0 °C was added with a syringe via a rubber septum after cooling at ice-water temperature (ca. 30 ml). Acetylene gas was allowed to bubble for two hours at 0 °C. The color of the reaction mixture rapidly changed to reddish red. After removal of CH_2Cl_2, the residue was dissolved in methanol, and then the insoluble OEPH$_2$ was filtered off. The filtrate was chromatographed on silica gel with CH_2Cl_2-acetone (10:1) the desired product **10a** as the second reddish red band in 91% yield: ^{1}H-NMR δ($CDCl_3$) 8.80 (singlet, 4H, *meso*-H of *Co*-vinyl porphyrin), 9.06, 10.41 (singletx2, 2Hx2, *meso*-H of *N*-vinyl porphyrin), 3.09, 3.22, 3.96x2, 4.29, 4.47, 4.46 (doublet of quartetx8, 2Hx8, CH_2CH_3 of *N*-vinyl porphyrin), 3.64 (multiplet, 16H, CH_2CH_3 of *Co*-vinyl porphyrin), 0.67, 1.81, 2.06, 2.13 (tripletx4, 3Hx4, CH_2CH_3 of *N*-vinyl porphyrin), 1.55 (triplet, 24H, CH_2CH_3 of *Co*-vinyl porphyrin), -4.79, -10.34 (doubletx2, 1Hx2, bridge vinyl-H J_{trans}=11.7Hz); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 383(5.30), 551(4.38) ; Anal. Calcd for $C_{74}H_{92}N_8O_4ClCo$: C,70.99; H,7.41; N,8.95. Found. C,70.79; H,7.28; N,8.84.

Co,N'-(CH=CH)(OEPCo^{III})(TPPH$_2$)ClO$_4$ **10b**; The reaction was performed by using $TTPH_2$ instead of $OEPH_2$ and worked-up according to the above procedure to afford **10b** in 77% yield: ^{1}H-NMR δ($CDCl_3$) 8.89 (singlet, 4H, *meso*-H of *Co*-vinyl porphyrin), 6.79, 8.85, 8.50, 9.08 (singletx2, doubletx2, 2Hx4, β-pyrrole), 3.94 (doublet of quartet, 16H, CH_2CH_3 of *Co*-porphyrin), 1.55 (triplet, 24H, CH_2CH_3 of *Co*-porphyrin), 7.23x2, 7.74, 8.00 (doubletx3, 4Hx1, 2Hx2, *meso-o*-Ph), 7.43x2, 8.09, 8.98 (doubletx3, 4Hx1, 2Hx2, *meso-m*-Ph), 2.69, 2.90 (singletx2, 6Hx2, *meso-p*-Me), -9.65, -3.16 (doubletx2, 1Hx2, bridge vinyl-H J_{trans}=11.7Hz); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 390(5.06), 447(4.96), 551(4.17), 623(3.94), 659(3.97); Anal. Calcd for $C_{84}H_{92}N_8O_4ClCo$: C,64.6; H,5.94; N,7.17. Found. C,72.81; H,5.18; N,7.29.

Co,N'-(CH=CH)(TTPCo^{III})(TTPH$_2$)ClO$_4$ **6c**; The reaction was performed by using $OEPH_2$ and (TTP)Co^{III}(H_2O)$_2$ClO$_4$ (**1b**) and worked-up according to the above procedure to afford **8b** in 36% yield: ^{1}H-NMR δ($CDCl_3$) 9.37, 10.20 (singletx2, 2Hx2, *meso*-H), 8.05 (singlet, 8H, β-pyrrole), 3.39, 3.82, 4.20, 4.23 (doublet of quartetx4, 4Hx4, CH_2CH_3), 0.81, 1.60, 1.89, 1.93 (tripletx4, 6Hx4, CH_2CH_3), 2.78 (singlet, 12H, *meso-p*-Me), -3.93, -9.63 (doubletx2, 1Hx2, bridge vinyl-H, J_{trans}=11.5Hz), 7.2~7.8 (multiplet, 16H, *meso*-Ph) -7.51 (broad, 1H, NH); UV-Vis(CH_2Cl_2) λ_{max} (log ε) 396(5.51), 533(4.61); Anal. Calcd for $C_{84}H_{92}N_8O_4ClCo$: C,64.6; H,5.94; N,7.17. Found. C,71.01; H,6.56; N,6.29.

Co,N'-(CH=CH)(TTPCo^{III})(TPPH$_2$)ClO$_4$ **6b**; The reaction was performed by using (TTP)Co^{III}(H_2O)$_2$ClO$_4$(**1b**) and $TTPH_2$ and worked-up according to the above procedure to afford 6b in 38% yield. Spectral data show before.

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Chapter IV

Hydrometallation of Alkenes, Alkynes, and Ethers via Hydridometalloporphyrins to Give Novel Organometalloporphyrins; Simulation of Intermediaries of Organometallic Macrocycles *in vivo*

Summary

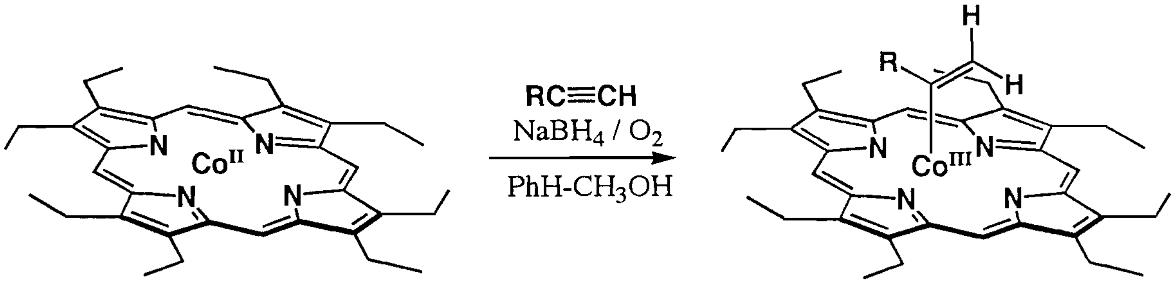
In the presence of sodium tetrahydroborate in large excess, octaethylporphyrinatocobalt(II), (OEP)Co^{II} (**1a**), reacted with various alkynes, alkenes, and ethers to give novel σ-vinyl and σ-alkylcobalt(III)porphyrins in good yields. These reactions required a limited amount of oxidant such as oxygen or peroxide. On the other hand, *meso*-tetraphenylporphyrinatoiron(III) chloride, (TPP)Fe^{III}Cl (**1b**), gave unique organoironporphyrins under the same conditions without requiring an oxidant. In the case of terminal alkynes, Schrock type carbene complexes were generated via the corresponding σ-vinyliron(III) porphyrins for the first time. Both organocobalt(III) porphyrins and organoiron(III) porphyrins were formed via the corresponding hydridometalloporphyrins. The key reaction process was assumed to be homolysis of hydrogen-metal bonding. In this chapter spectroscopic identification of these complexes and reaction mechanisms were described.

Introduction

Transition metal (Os, Mn, Fe, Co, Ni, Ru, Rh) complexes of porphyrins and related macrocycles have recently been demonstrated to catalyze hydroxylation[1] and epoxidation[2] of organic substrates in the presence of a reductant and molecular oxygen. Although these reactions are closely related to the monooxygenation reaction of cytochrome P-450 which is now believed to activate molecular oxygen as a form of oxenoid[3], activation of organic substrates to give organometallic intermediates is an alternative pathway to lead to catalytic oxygenation in some cases depending on the metal. So it is important to investigate the reactivities of metalloporphyrins toward organic substrates in the presence of both a reductant and a oxidant under similar reaction conditions to that *in vivo*. Our knowledge about the chemistry of vitamin B_{12} have accumulated. Several model complexes have recently been synthesized to investigate the nature of cobalt-carbon bonds which play an important role in the initial step of vitamin B_{12}-dependent reactions[5]. Thus, the versatile methodology to generate cobalt-carbon bonds has been of increasing importance in order to investigate vitamin B_{12}-dependent reactions. The formation of carbon-iron bond has been discovered in the enzymatic process, many groups have carried out the investigations on synthesis and properties of metal-iron bond. There are tree typical synthetic methods of σ-alkylmetalloporphyrin; i) the reaction of cationic metal(III) porphyrins with carbanion ii) the reaction of metal(II) porphyrins with radical iii) reaction of metal(I) porphyrins with alkylhride. This chapter describes the facile formation of organometalloporphyrins from alkynes, alkenes, and ethers by the use of the corresponding metalloporphyrins and sodium tetrahydroborate.

Results and Discussion

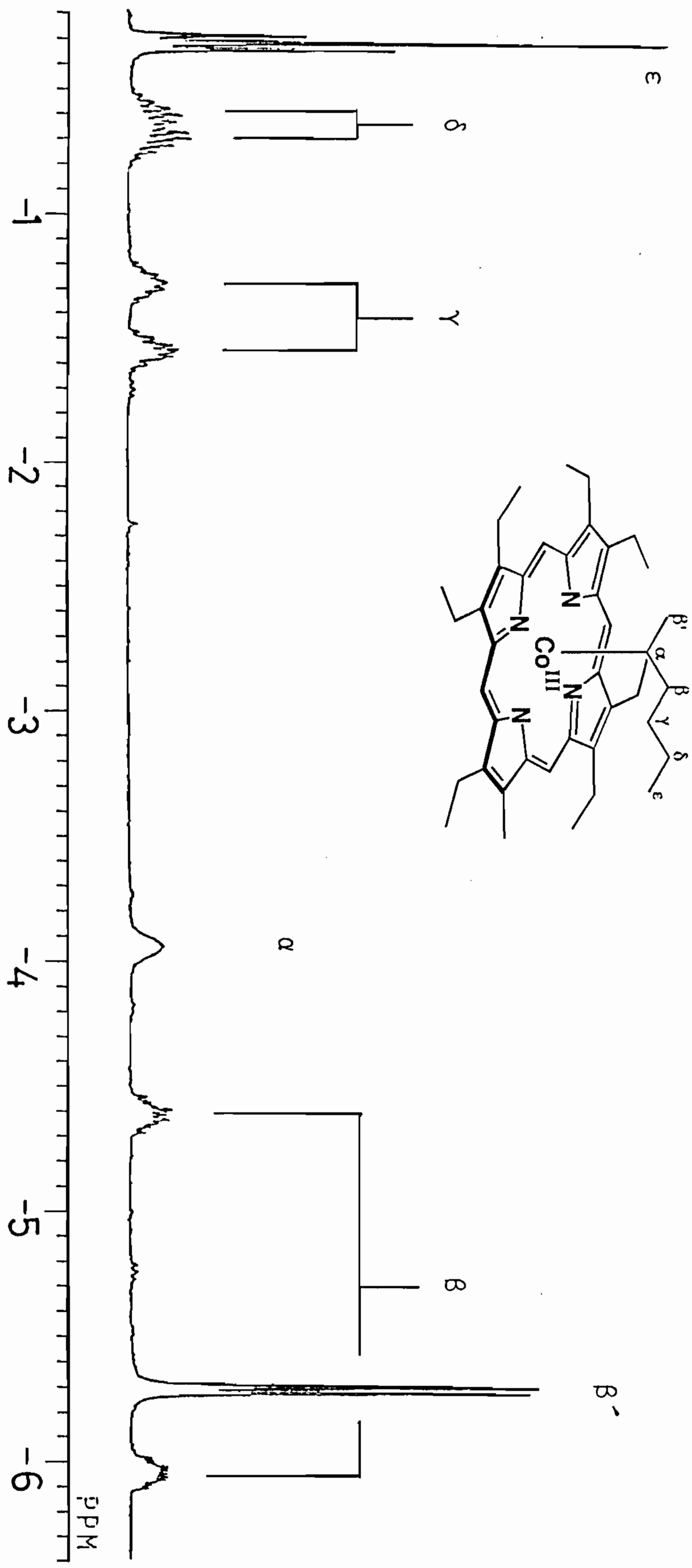
Synthesis and Identification of σ-(Vinyl)Co^{III} Porphyrins



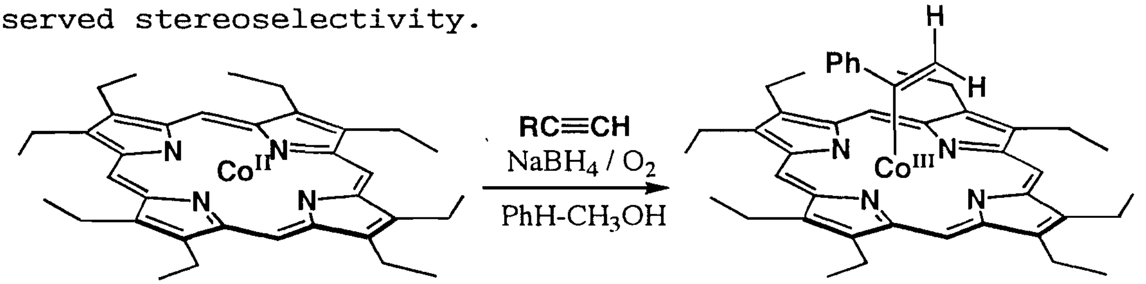
2; R=Ph
3; C_4H_9

Octaethylporphyrinatocobalt(II) (OEP)Co^{II} (**1a**) and $NaBH_4$ (ca. 30 eq.) were suspended in the mixture of benzene-methanol (12 ml : 0.4 ml) under argon atmosphere containing a limited amount of oxygen. Various alkynes, such as phenyl acetylene, 1-hexyne, 3-hexyne and 2-hexyne were added to the solution and stirred overnight at ambient temperature in the dark. This reaction was accelerated by the presence of oxygen. Indeed, reaction of **1a** with 1-hexyne was vigorously accelerated under aerobic atmosphere. The reaction mixture was evaporated and then extracted into benzene with removing (OEP)Co^{II} and $NaBH_4$ by filtration. Recrystallization from CH_2Cl_2-methanol afforded σ-alkyl cobalt(III) porphyrins (**2**-**6**). These complexes were quickly worked up in the dark because of the light-sensitive character.

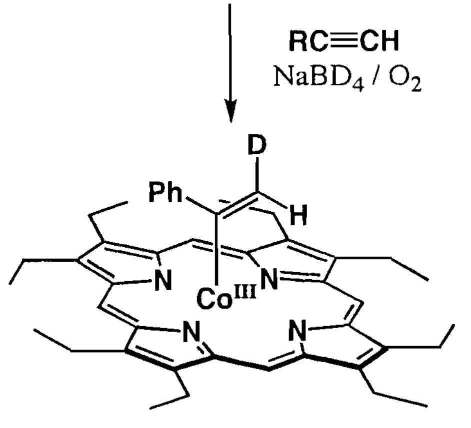
These complexes show similar UV-Vis spectra typical of σ-vinyl cobalt(III) porphyrins which show a Soret band (about 395 nm) and a two-banded Q-band at 520 nm and 550 nm. These structures were evidenced by the ^1H-NMR spectra. The coupling constants between up-field shifted signals due to vinylic protons at -2.67 and -0.83 ppm (J_{gem}=2.2 Hz) for **2** and at -3.12 and -0.96 ppm (J_{gem}=3.6 Hz) for **3** are in the range of typical *geminal* coupling. In general, up-field chemical shifts of σ-vinyl moieties in ^1H-NMR spectra are explained in terms of the porphyrin ring current effect. The proton near a porphyrin plane is greatly influenced by the porphyrin ring current effect. The peak at about -3 ppm is due to a β-*cis* proton, and the peak at about -1 ppm is due to a β-*trans* proton with respect to Co^{III}. The C_{4v} symmetry of the OEP ligand is confirmed by one singlet at about 10.0 ppm due to *meso*-H, one doublet of quartets at about 4.0 ppm due to methylene-H, and one triplet at about 1.9 ppm due to methyl-H, with 1:4:6 integration intensity. This hydrometallation of terminal alkynes is regioselective to give Markownikoff type products, **2** and **3**. Internal alkynes gave a mixture of some isomers. In the case of 3-hexyne, one set of signals at -4.44, -3.02, -1.77, -1.05 and -0.80 ppm due to the axial organo ligand with 2:2:3:3:1 integration intensity were assigned to (*Z*)-σ-(hex-3-en-3-yl)cobalt(III) porphyrin (**4a**), while another set of signals at -3.58, -2.61, -0.96, and -0.20 ppm with 1:3:3:2 integration intensity were assigned to (*E*)-σ-(hex-3-en-3-yl)cobalt(III) porphyrin (**4b**) in a detailed comparison with the ^1H-NMR data of σ-(hex-1-en-2-yl)cobalt(III) porphyrin (**3**). Since the β-*cis* and β-*trans* proton with respect to Co^{II} vinyl protons were observed at -3.12 and -0.96 ppm, respectively, signals at -0.80 and -3.58 ppm due to the vinyl proton of **4a** and **4b** were associated with the


ε
δ
γ
α
β
β'
N
N
N
N
Co^III
β'
α
β
γ
δ
ε
-1
-2
-3
-4
-5
-6
PPM

β-*trans* and β-*cis*, respectively. That is, the complex **4a** is in a *Z* form and the complex **4b** is *E* form. The ratio of *E* and *Z* form was 1:4 on the basis of their ^{1}H-NMR signal intensities. On the occasion of 2-hexyne, a mixture of four isomers were afforded by the above experiment. The most major product was (*E*)-σ-(hex-2-en-2-yl)cobalt(III) porphyrin (**5a**) on the basis of integration intensity of β-vinyl protons. The ratio of stereoselectivity (*E* or *Z*)(1:3 ratio) and regioselectivity (2- or 3-)(3:2 ratio) was calculated on the basis of ^{1}H-NMR spectral data. As far as internal alkynes were concerned, *trans*-addition of hydrogen and cobalt were preferred to *cis*-addition of these, in spite of the steric hindrance between the porphyrin plane and β-CH_2 or β-CH_3 substituents. This implies that the Co^{III}-C bond forming process is not responsible for the observed stereoselectivity. The stabilities of forming alkyl radical is responsible for the observed stereoselectivity.

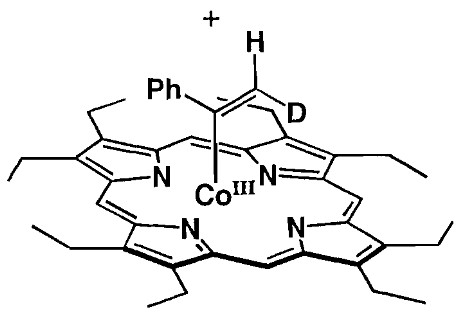


2

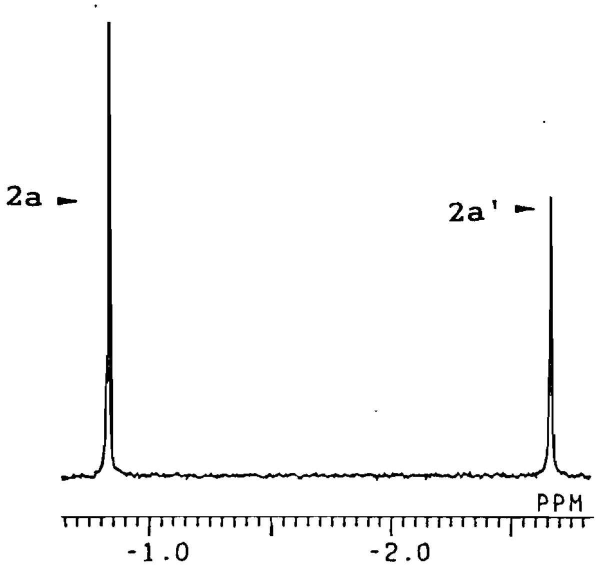


2a; *trans* add.

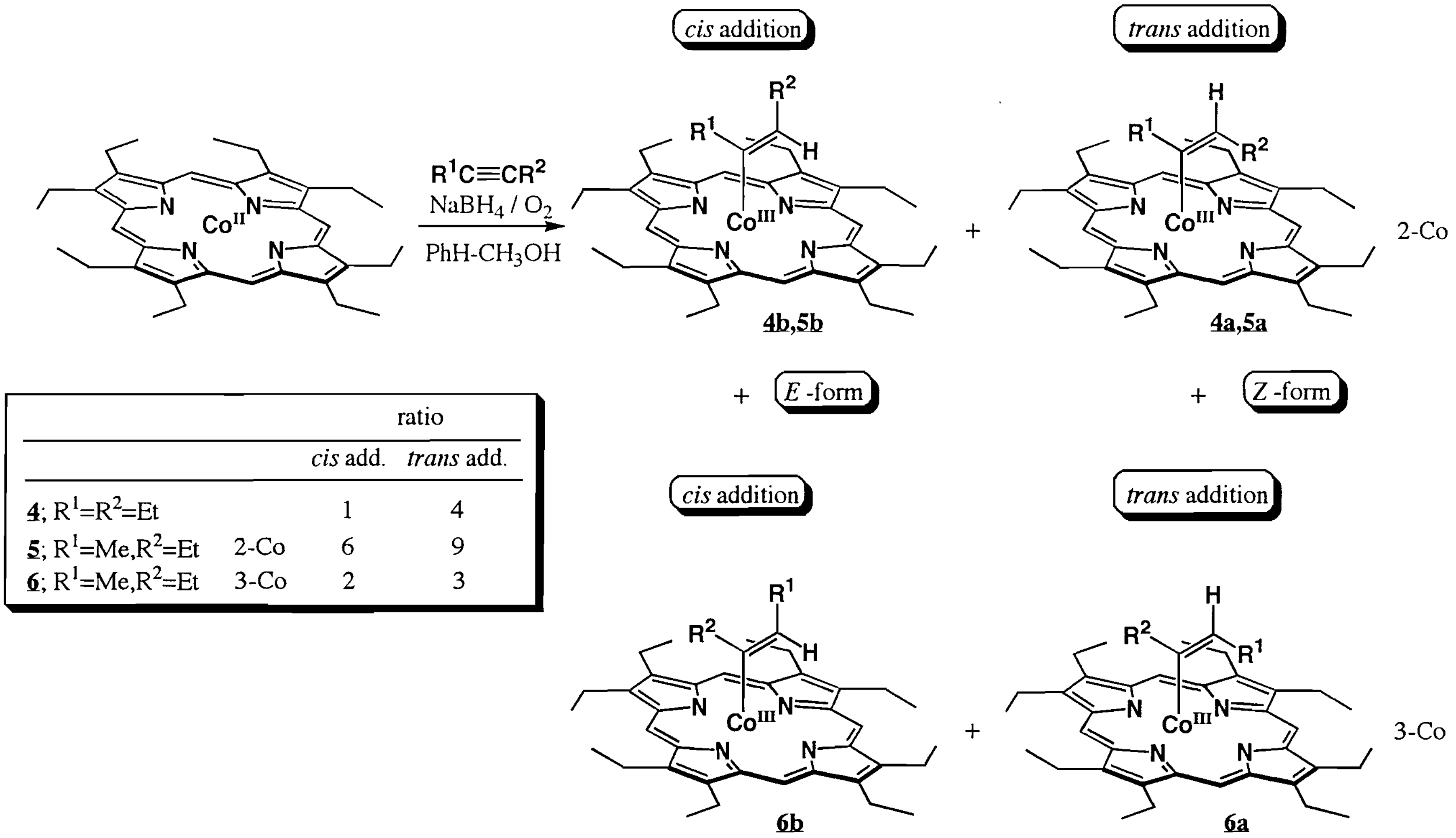
+



2a'; *cis* add.



2a :**2a'** = 8: 5



		ratio	
		cis add.	*trans* add.
4; R^1=R^2=Et		1	4
5; R^1=Me,R^2=Et	2-Co	6	9
6; R^1=Me,R^2=Et	3-Co	2	3

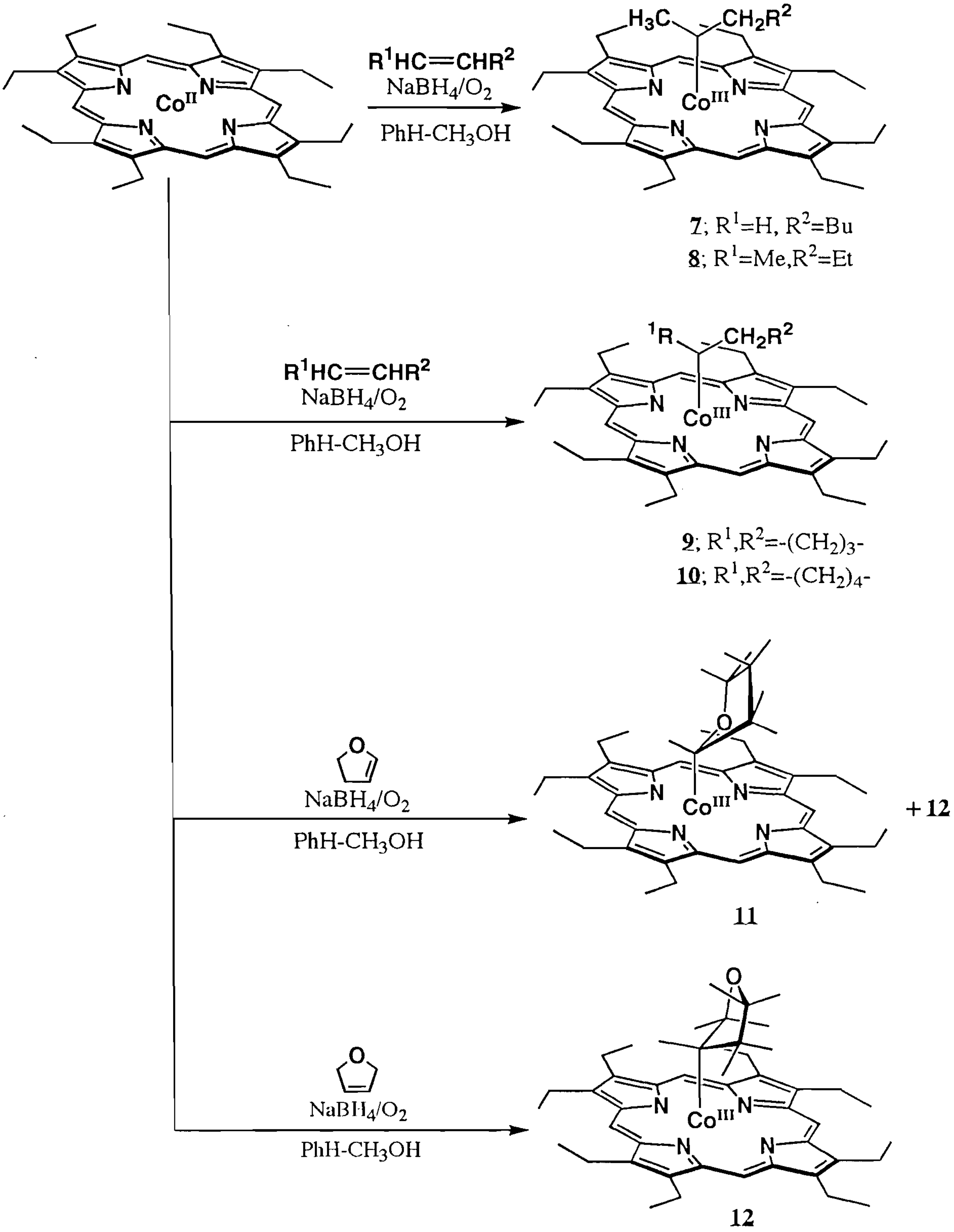
Although exactly one deuteride was incorporated into the organocobalt(III) porphyrins (**2a**,**2a'**) which was derived from the reaction of **1a**, phenyl acetylene, and $NaBD_4$ for the purpose of investigating the stereochemical feature of these reactions. However, the two singlets due to the vinylic protons at -2.67 and -0.83 ppm observed in the ^1H-NMR spectrum of a mixture of **2a** and **2a'** indicates that both *cis* and *trans* addition of deuteride and cobalt are occurring with 8:5 ratio. This fact is inconsistent with a concerted reaction mechanism such as hydroboration of terminal alkynes followed by metathesis.

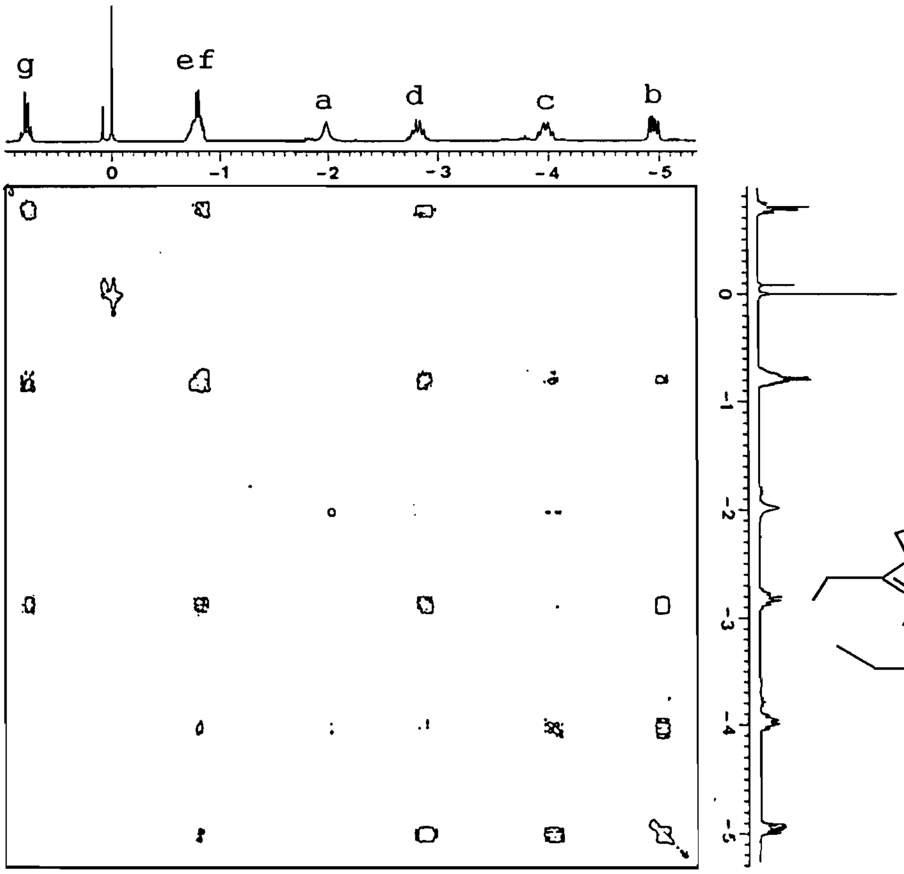
Synthesis and Identification of σ-(Alkyl)Co^{III} Porphyrins

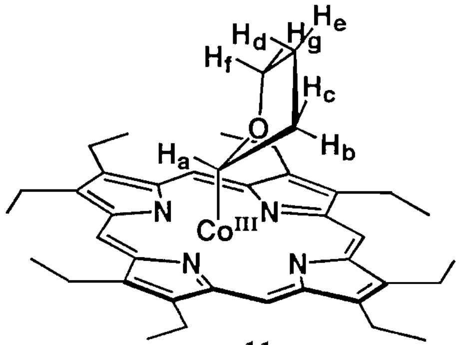
Compound **1a** reacted also with various alkenes such as 1-hexene, 2-pentene, cyclopentene, cyclohexene, 2,5-dihydrofuran, 2,3-dihydrofuran, and allylbenzene in the above procedure to give the organometallic complexes **7-13**. Hydrometallation of 1-hexene and 2-pentene using (OEP)Co^{II} and $NaBH_4$ afforded σ-(1-methylpentyl)Co^{III}(OEP) (**7**) and σ-(1-methylbutyl)Co^{III}(OEP) (**8**) in 83% and 68% yields, respectively, without 1-hexyl and 3-pentyl isomers. Cyclohexene, cyclopentene, 2,5-dihydrofuran and 2,3-dihydrofuran (pretreated with active aluminum oxide, to remove a stabilizer which is contained as a radical scavenger) also afforded novel σ-cycloalkylcobalt(III) complexes (**9-12**) in the yields of 68-91%. The structure of the compound **9** was confirmed by the alternative synthesis[5] from the reaction of bromocyclopentane with (OEP)Co^I. 2-Methyl-1-pentene and methyl acrylate did not react at all. It is important to point out that anionic cobalt(I) complexes and hydridocobalt(III) complexes with other macrocyclic ligands react most readily with electron-deficient alkenes[6].

The UV-Vis spectra of **7-13** exhibits absorption maxima typical of σ-alkyl cobalt(III) porphyrin at about 390 and 550 nm.

The ^1H-NMR spectra of these complexes widely show up-field shifted signals. A signal of doublet at about -6 ppm due to the β-methyl protons of the complexes **7** and **8** indicats the formation

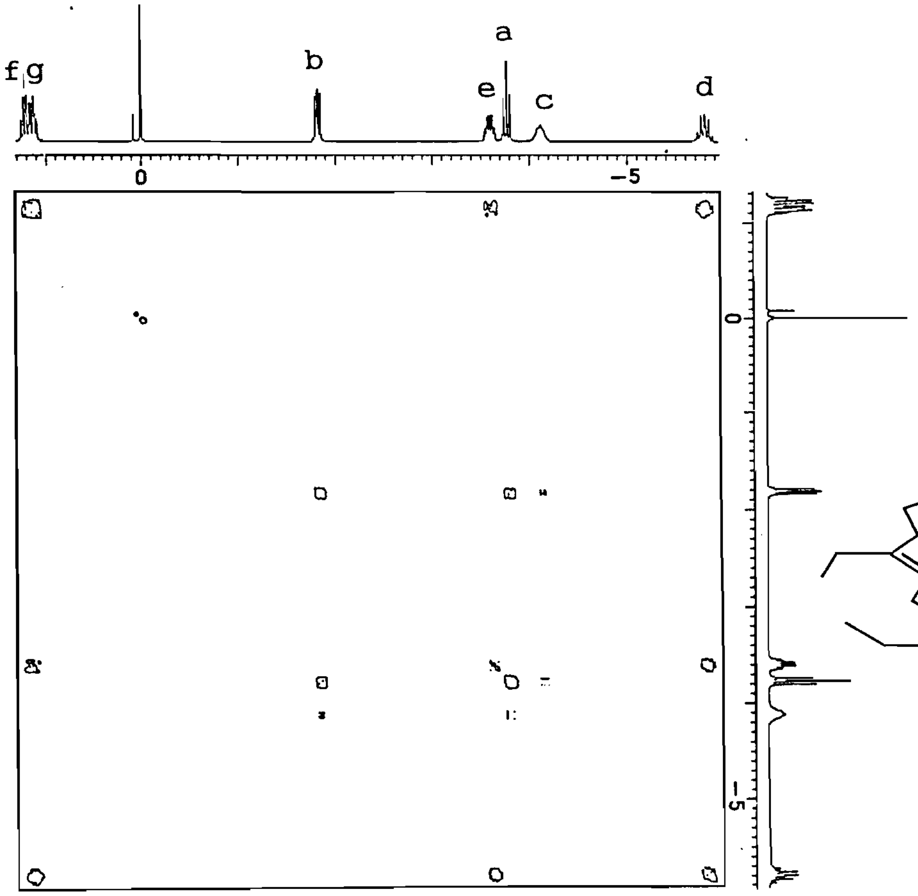

Co^{II}
$R^1HC{=}CHR^2$
$NaBH_4/O_2$
PhH-CH_3OH
H_3C
CH_2R^2
Co^{III}
7; R^1=H, R^2=Bu
8; R^1=Me,R^2=Et
$R^1HC{=}CHR^2$
$NaBH_4/O_2$
PhH-CH_3OH
^1R
CH_2R^2
Co^{III}
9; R^1,R^2=-$(CH_2)_3$-
10; R^1,R^2=-$(CH_2)_4$-
O
$NaBH_4/O_2$
PhH-CH_3OH
O
Co^{III}
11
+ 12
O
$NaBH_4/O_2$
PhH-CH_3OH
O
Co^{III}
12

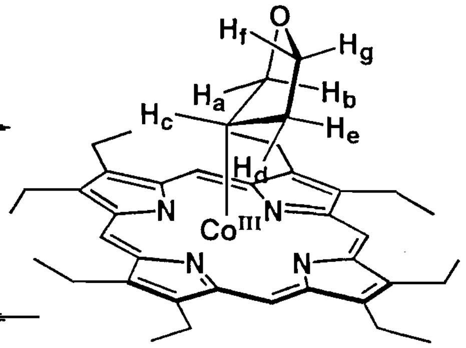




11

Figure 4-1. 2D-COSY Spectra of Compound **11**





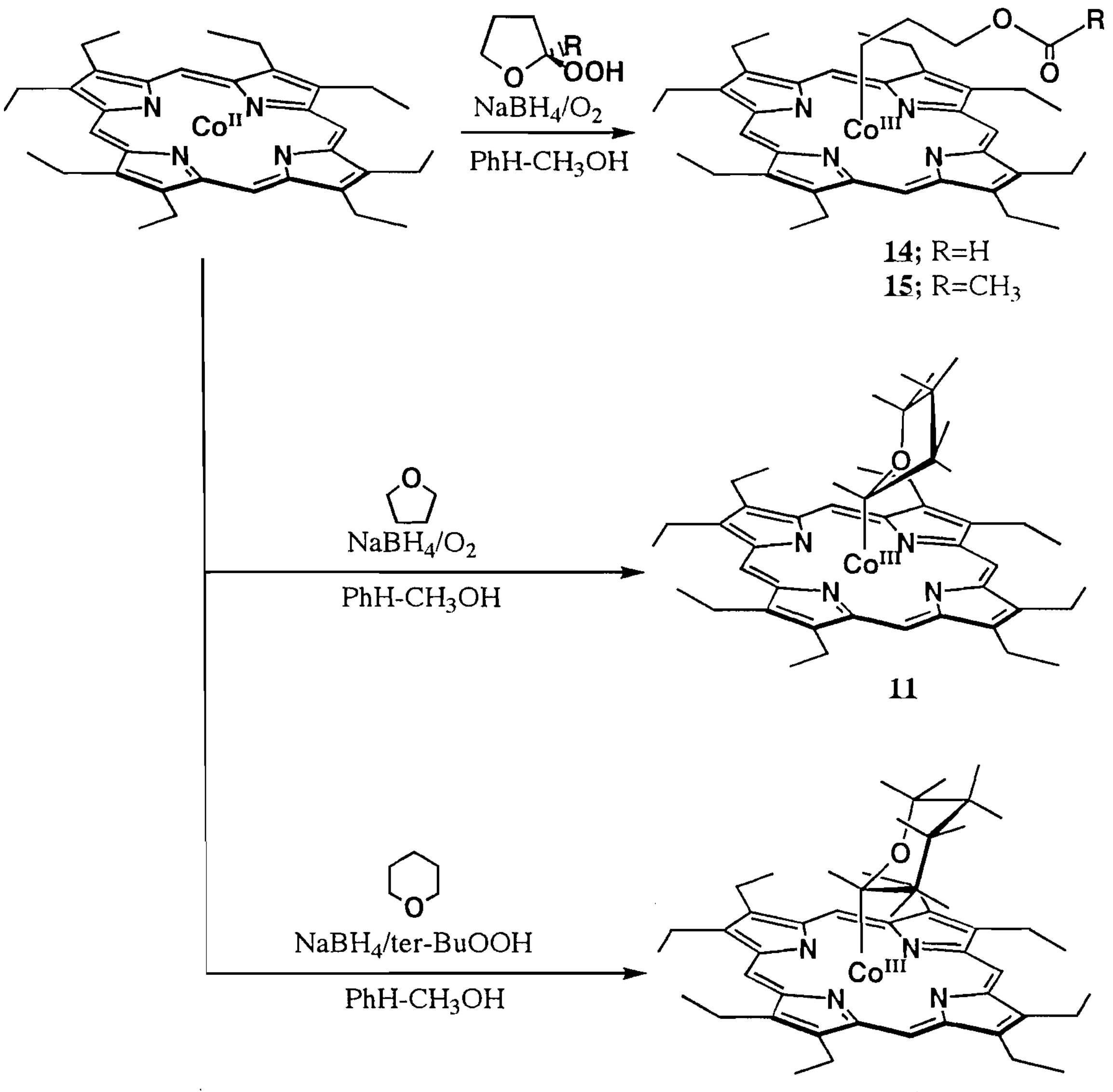
12

Figure 4-2. 2D-COSY Spectra of Compound **12**

of σ-1-methylalkyl complexes. The α-methine proton which is magnetically coupled with the nuclear spin of the cobalt atom (I=7/2) is observed as a broad signal at about -4 ppm. The chiral α-methine center gives rise to a great magnetic anisotropy towards β-, γ- and δ-positions of the σ-alkyl moieties. Thus, each proton at the β-, γ-, and δ-positions of σ-alkyl moieties was observed as a discrete signal. The OEP ligand with a C_{4v} symmetry is confirmed by one singlet at about 10.0 ppm due to *meso*-H, one doublet of quartets at about 4.0 ppm due to methylene-H, and one triplet at about 1.9 ppm due to methyl-H, with 1:4:6 integration intensity. The signals of tetrahydrofuranyl moieties are easily analyzed on the basis of the ring current effect and coupling patterns to differentiate **11** and **12**. The α-methine proton of **11** appeared at -1.99 ppm and that of **12** appeared at -3.05 ppm. The above α-methine protons of these two complexes appear as broad signals at quite different chemical shifts due to the inductive effect of oxygen. The latter is metallated at the α-position of THF and the former at the β-position of THF. The correlations to the α-methine proton were traced in the 2D-COSY spectra of **11** and **12** to make assignments of other protons of σ-alkyl groups. The rigid tetrahydrofuranyl substituents have some sets of vicinal protons whose dihedral angle is ca. 90 degree. That is, the correlation of some adjacent protons is not observed in the 2D-Cosy NMR spectra as shown in Figure 4-1, and 4-2. ^{13}C-NMR spectral data of σ-(2-tetrahydrofuranyl)Co^{II}(OEP), **12**, indicated that the α-methine carbon directly bonded to cobalt was not observed in the ^{13}C-NMR due to the quadrupolar relaxation effect to the nuclear spin of cobalt atom (I=7/2).

The reactivity and the direction of the addition of cobalt and hydrogen to a carbon-carbon double bond depend on the substitution pattern of alkenes. Electron-donating substituents promote hydrometallation with the cobalt introduced into the more substituted end of olefins as is shown in the reaction of 1-hexene. This corresponds to a Markownikoff type addition. However, 2,3-dihydrofuran exceptionally gave two isomeric products **11** and **12** in 87% total yield with 1:1 ratio. The disubstituted end of 2-methyl-1-pentene was not available for the bonding with cobalt probably due to the steric constraint which, in turn, enables differentiation between the methyl and the ethyl substituted ends of 2-pentene to generate **8** exclusively.

Reactions in the Presence of Hydroperoxides



14; R=H
15; R=CH$_3$

11

16

The above reactions require assistance by a limited amount of oxidant. So the aged THF and 2-methylTHF containing 2-hydroperoxides were reacted with **1a** in the presence of NaBH$_4$. The 2-

hydroperoxides gave σ-(γ-formoxypropyl)cobalt(III) porphyrin (**14**) and σ-(γ-acetoxypropyl)cobalt(III) porphyrin (**15**) in 93% and 50% yields, respectively. These hydroperoxides were decomposed to generate alkoxy radicals which undergo ring opening rearrangement with carbon-carbon bond cleavage to γ-acyloxypropyl radicals and then combine with **1a** to give σ-(alkyl)cobalt(III) porphyrin complexes.

UV-Vis spectra of these complexes are typical of σ-alkyl cobalt(III) porphyrins with a Soret band at about 398 nm and a two-banded Q-band at 520 nm and 550 nm. The IR spectra of **14** showed intense absorptions due to the acyloxyl group at 1730, 1350 cm^{-1}. ^{1}H- and ^{13}C-NMR spectral data of **14** gave evidence in support of this structure. The spectral properties of **14** completely conformed with those of the material obtained from the reaction of $(OEP)Co^{I}$ with 1-bromopropylacetate.

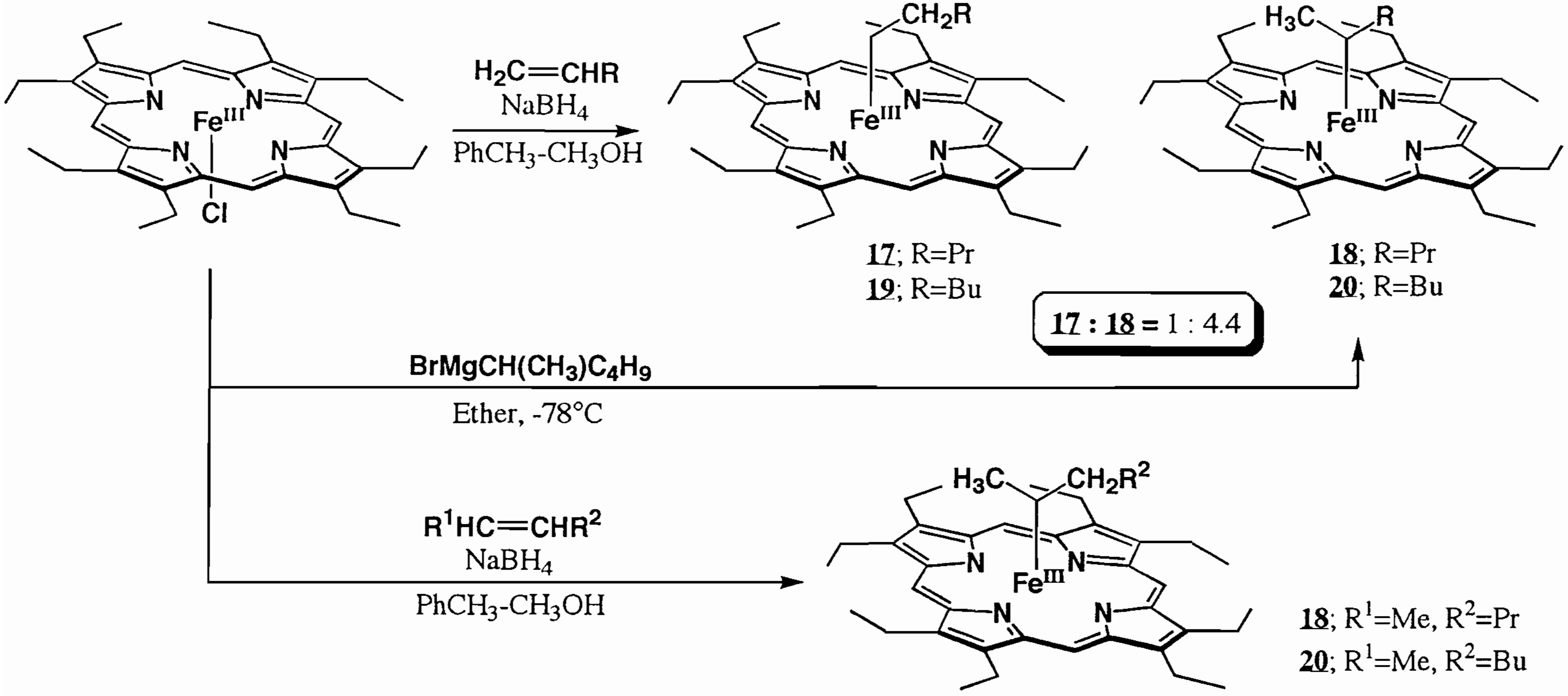
When **1a** was allowed to react with $NaBH_4$ in tetrahydrofuran at ambient temperature under argon atmosphere for 12 hours, the α-methylene position of THF was effectively metallated to give σ-(α-tetrahydrofuranyl)cobalt(III) porphyrin (**12**) in 75% yield. A similar reaction of tetrahydropyran instead of THF gave no product. But, interestingly, this reaction was greatly accelerated and reached to completion within 15 minutes by the addition of *tert*-butylhydroperoxide to give σ-(2-tetrahydropyranyl)-cobalt(III) porphyrin (**16**) in 75% yield. The reaction with THF was also accelerated by the addition of *tert*-butylhydroperoxide. However, addition of *tert*-butylhydroperoxide did not promote hydrogen abstraction from allylic position of 1-hexene and allylbenzene but did accelerate hydrometallation of these allylic substrates to form **8** and σ-(1-phenyl-2-propyl)cobalt(III) porphyrin (**13**). Whereas σ-(alkyl)cobalt(III) porphyrins have so far been prepared through the tedious procedure using anionic Co^{I} species, the present reactions provide quite simple method for these organocobalt(III) porphyrins with a secondary alkyl σ-ligand which are difficult to obtain by the other methods. Furthermore, this work indicates that some catalytic processes using cobalt porphyrin may be realized if σ-(alkyl)cobalt(III) intermediates can be transformed efficiently.

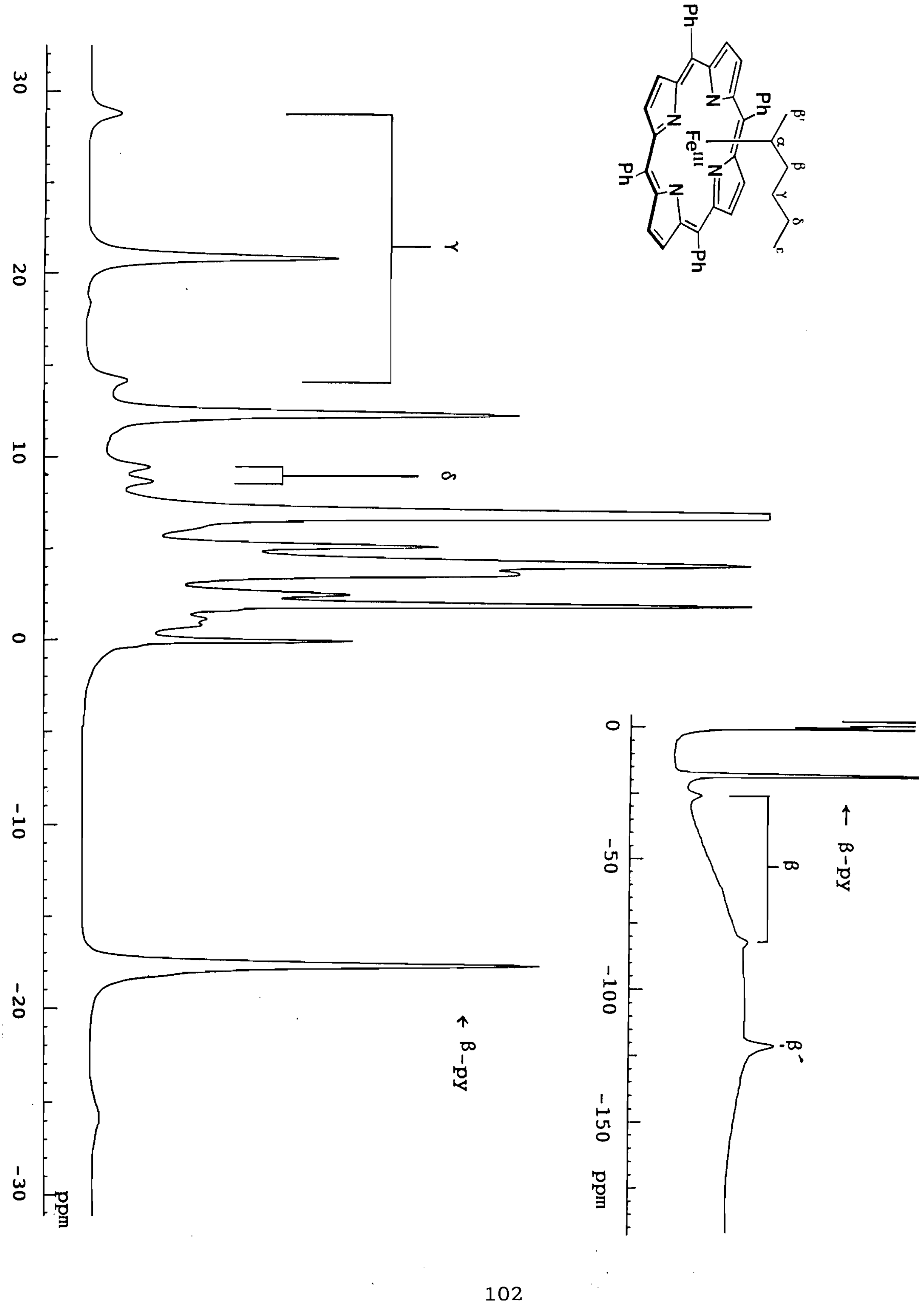
Reaction of (TPP)Fe^{III}Cl with Alkenes in the Presence of NaBH$_4$

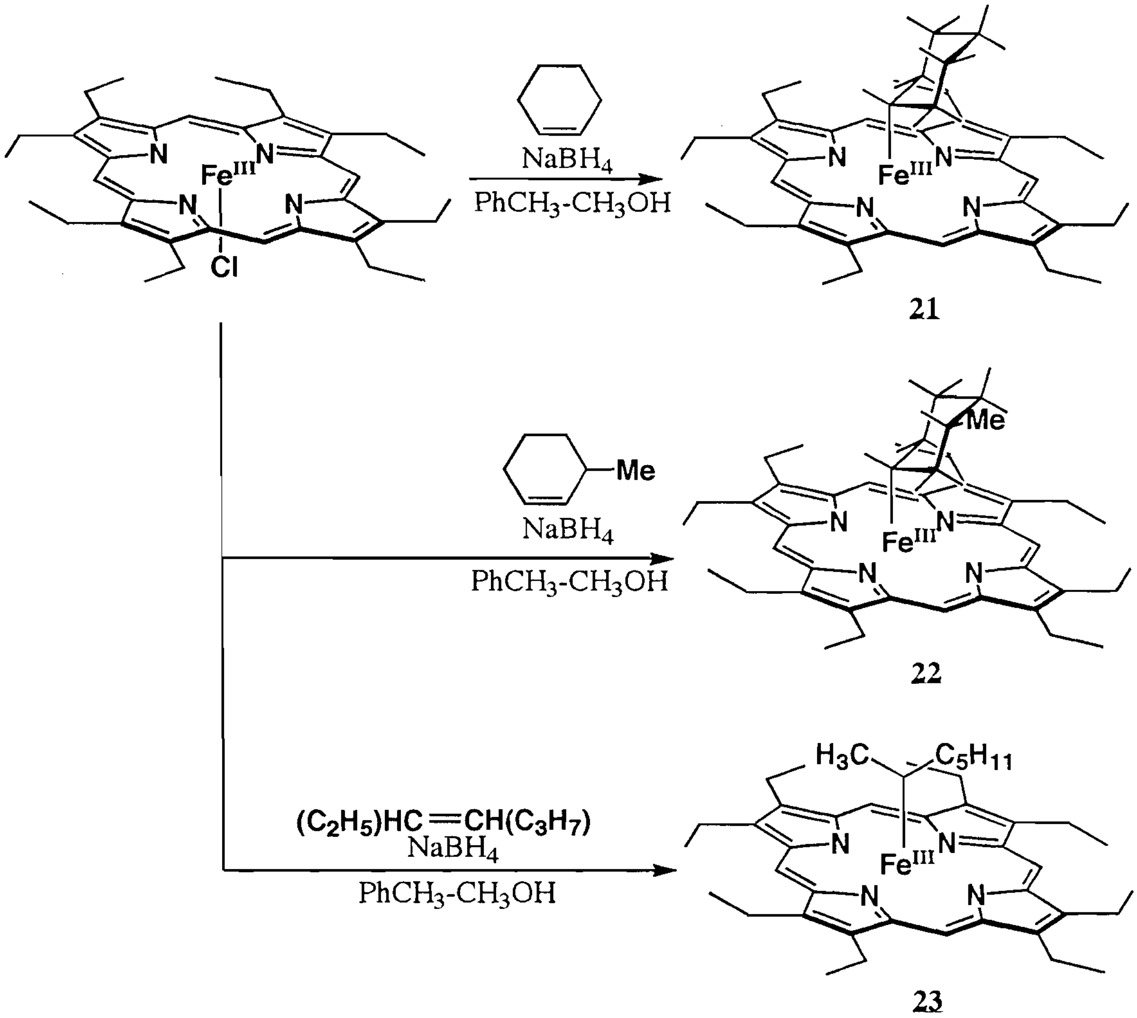
Meso-tetraphenylporphyrinatoiron(III) chloride, (TPP)Fe^{III}Cl (**1b**) and various alkenes, such as 1-pentene, 1-hexene, 2-pentene, 2-hexene, 3-heptene, cyclopentene, cyclohexene, and 3-methylcyclohexene, in the presence of NaBH$_4$ were reacted in the mixture of toluene-methanol (10 ml:0.2 ml) under argon atmosphere. The color of the solution changed from brown to red in a few minutes. The resulting compounds were so sensitive against light and air that the following treatments were performed under argon atmosphere in the dark. The solvent was completely removed under vacuum for several hours and the residue was extracted with degassed d$_6$ benzene. The degassed d$_6$ benzene extract was purified by quickly passing through a short column of basic alumina and immediately analyzed by ^{1}H-NMR spectroscopey.

1-Pentene gave a mixture of σ-(pentyl)Fe^{III}(TPP) (**17**) and σ-(1-methylbutyl)Fe^{III}(TPP) (**18**) in a ratio of 1:4.4 on the basis of the signal intensity of β-pyrrole protons. 1-Hexene gave a mixture of σ-(hexyl)Fe^{III}(TPP) (**19**) and σ-(1-methylbutyl)-Fe^{III}(TPP) (**20**) in a ratio of 1:8.2. Signals due to (TPP)Fe^{II} and [(TPP)Fe^{III}]$_2$O were also slightly observed. 2-Pentene and 2-hexene gave σ-(1-methyl-1-alkyl)Fe^{III}(TPP) without regioisomers in a detectable amount under the same reaction conditions. Cyclohexene and 3-methyl-1-cyclohexene gave σ-(cycloalkyl)-Fe^{III}(TPP) (**21**, **22**). Furthermore, σ-(1-methylhexyl)Fe^{III}(TPP) (**23**) was found to be the sole organoiron(III) porphyrin product when 3-heptene was allowed to react in a similar manner.

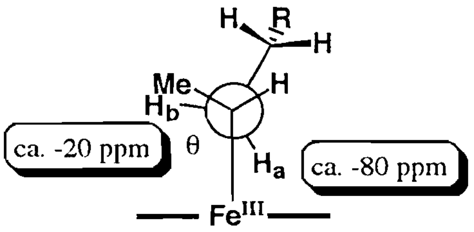
The structures of these σ-type organo iron(III) porphyrins were determined with referring to the ^{1}H-NMR chemical shifts of σ-(ethyl)Fe^{III}(TPP) and σ-(butyl)Fe^{III}(TPP) reported by P. Cocolios[7] and σ-(1-adamantyl)Fe^{III}(TPP) and σ-(4-camphyl)Fe^{III}(TPP) reported by A. L. Balch.[8] The spectral properties of **19** completely coincided with those of the material obtained from the reaction of **1b** with 1-methylpentyl magnesium bromide. The TPP


Fe^{III}
Cl
$H_2C{=}CHR$
$NaBH_4$
$PhCH_3$-CH_3OH
CH_2R
17; R=Pr
19; R=Bu
H_3C
R
18; R=Pr
20; R=Bu
17 : 18 = 1 : 4.4
$BrMgCH(CH_3)C_4H_9$
Ether, -78°C
$R^1HC{=}CHR^2$
$NaBH_4$
$PhCH_3$-CH_3OH
H_3C
CH_2R^2
18; R^1=Me, R^2=Pr
20; R^1=Me, R^2=Bu


Ph
Ph
Ph
Ph
N
N
N
N
Fe^{III}
β'
α
β
γ
δ
ε
γ
δ
← β-py
β
β'
← β-py
30
20
10
0
-10
-20
-30
ppm
0
-50
-100
-150
ppm

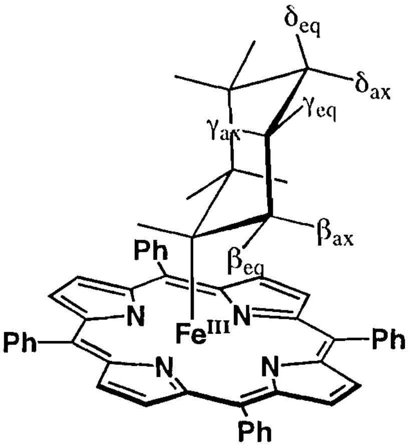


ligand with a C_{4v} symmetry is confirmed by signals at about -18 ppm due to the β-pyrrole protons and at the region from 2 to 8 ppm where the phenyl protons resonate. σ-(1-Methylalkyl)Fe^{III}(TPP) complexes showed a 3-H signal at a region (ca. -120 ppm) characteristic of a β-methyl group with respect to Fe. The signals at about -80 and -20 ppm were assigned to the β-CH_2 protons on the basis of their intensity and line width. The average of -80 ppm and -20 ppm is close to the chemical shift -63.7 ppm of the β-CH_2 of σ-(propyl)Fe^{III}(TPP) reported by P. Cocolios. Furthermore, the chiral center gives rise to great magnetic anisotropy towards β-, γ-, and δ-protons of σ-alkyl moieties. The chemical shift difference between two β-CH_2 protons is particularly large (ca. 60 ppm). The ^{1}H contact shifts which arise from interaction of the nucleus of interest with the unpaired electron *via* delocalization of the spin into an orbital centered on the nucleus are sensitive to conformation. The isotopic shift for these β-CH_2 protons mainly of a contact origin are dependent on the dihedral angle between the $HC_{\alpha}C_{\beta}$ and $C_{\beta}C_{\alpha}Fe$ planes just like a *vicinal* coupling constant in diamagnetic ^{1}H-NMR. The dipolar contribution which was estimated by A.L.Balch was about 47 ppm at the β-methylene protons at 20 °C. Since the dipolar terms in the isotropic shifts of H_a and H_b are almost the same size, the contact terms are estimated to be -122 and -68 ppm taking the chemical shifts of the corresponding cobalt(III) complex (**8**) as references. Because the dihedral angle [$\angle$(Fe-C-C-H_a)] is less than 60 degree while that [$\angle$(Fe-C-C-H_b)] is more than 60 degree due to the steric repulsion between the β'-CH_3 and the γ-CH_2R group, the resonances at around -80 ppm are associated to H_a and those at around -20 ppm are associated to H_b.



$$\frac{A}{h} = (B_0+B_2\cos^2\theta)\,\frac{\rho_c}{2S}$$

The rigid σ-cyclohexyle moiety of the complex (**21**) showed signals at 16.2 and -12.8 ppm which are assigned to the δ-H_{ax} and δ-H_{eq} protons, respectively. This assignment is based on the reported chemical shifts of δ-H_{ax} (10.3 ppm) and δ-H_{eq} (-20.8 ppm) in the σ-(1-adamantyl)Fe^{III}(TPP) (**A**). The broad 2H-signal at -20.8 ppm of **21** indicative of its close vicinity to iron is probably associated with the β-H_{eq}. The β-H_{ax} protons were too broad to be detected at room temperature. But, the β-H_{ax} and β-H_{eq} appeared at -19.8 and -12.4 ppm at -25 °C, respectively. the remaining two sharp 2H-signals at -30.4 and 34.1 ppm were assigned to γ-H_{eq} and γ-H_{ax} protons, respectively, because the γ-H_{eq} protons of **A** resonate at -14.4 ppm. The isotopic shifts of



$$\left(\frac{\Delta H}{H}\right)^{iso} = \left(\frac{\Delta H}{H}\right)^{dip} + \left(\frac{\Delta H}{H}\right)^{con}$$

$$\left(\frac{\Delta H}{H}\right)^{dip} = \frac{[\beta^2 s(s+1)(g^2_{//}-g^2_{\perp})(3\cos^2\theta-1)]}{9kTr^3}$$

Table 4-1. Separation of Chemical Shifts into Contact and Dipolar Contributions for σ-(Cyclohexyl)Fe^{III}(TPP) (benzene-d_6 at 23°C)

Protons	GF[a)]	$\left(\frac{\Delta H}{H}\right)^{obs.}$	$\left(\frac{\Delta H}{H}\right)^{ref.^{b)}}$	$\left(\frac{\Delta H}{H}\right)^{iso.}$	$\left(\frac{\Delta H}{H}\right)^{dip.}$	$\left(\frac{\Delta H}{H}\right)^{con.}$
β_{eq}	$1.69\text{x}10^{-2}$	-20.8	-5.1	-15.7	28.8	-44.5
β_{ax}	$1.69\text{x}10^{-2}$	c)				
γ_{eq}	$1.17\text{x}10^{-2}$	-30.4	-1.0	-29.8	19.9	-49.7
γ_{ax}	$1.65\text{x}10^{-2}$	34.1	-1.2	35.5	46.4	-10.9
δ_{eq}	$0.87\text{x}10^{-2}$	-12.8	-0.3	-12.5	14.8	-27.3
δ_{ax}	$1.25\text{x}10^{-2}$	16.2	-0.3	17.1	21.3	-4.2

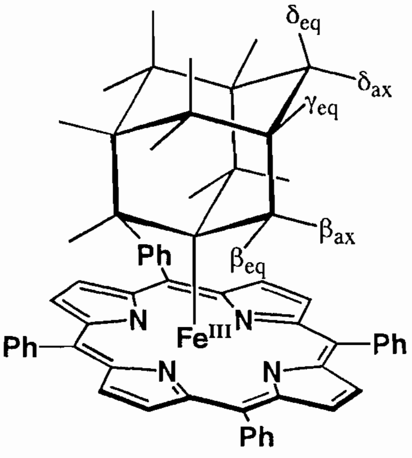
a) Geometric facter was calculated assuming the Fe-C distance of 2.25 angstrom.

b) Diamagnetic reference chemical shifts were taken from the data for σ-(cyclohexyl)Co^{III}(OEP).

c) Too broad to be detected at 23°C, but β_{eq} and β_{aq} protons appeared at -19.8 and -12.4 ppm at -25°C

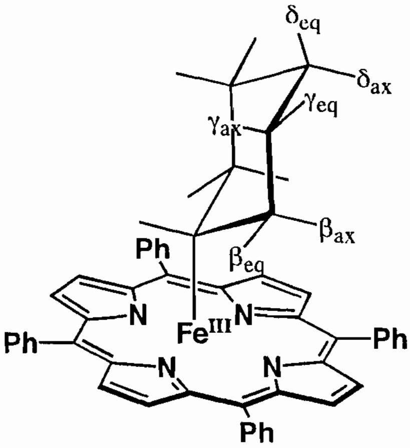
the cyclohexyl protons are separated into contact and dipolar contribution by using parameters used for the analysis of the complex **A**.[8] Table 4-1 indicates that the contact term of the *equatorial* protons are generally larger than those of the axial protons. For example, the contact term for the γ-H_{eq} is -49.7 ppm while that for the γ-H_{aq} is -10.9 ppm. This tendency is explainable in terms of the dihedral angle dependency of the spin delocalization through the σ-bonds framework as noted previously.

Table4-2. Chemical Shifts σ-(Cycloalkyl)Fe^{III}(TPP) Complexes (benzene-d_6 at 23°C)



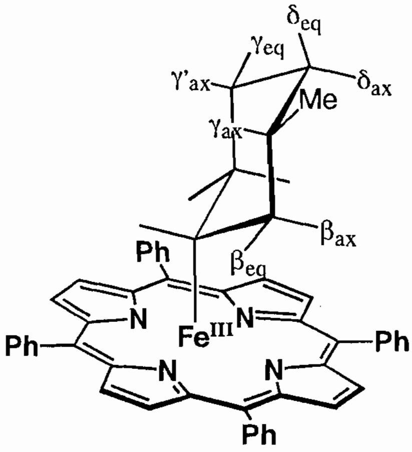
A

Reported by A. L. Balch
(1990)



21

	A	21	22
Temp.	20	23	23
β-pyr	-18.4	-18.3	-18.2
β_{eq}	-19.8	-20.8	-22.2 -23.4
β_{ax}	-19.8	b)	-11.8 -14.2
γ_{eq}	-14.4	-30.4	-35.0
γ_{ax}		34.1	34.0 36.1
δ_{eq}	-20.8	-12.8	-10.3
δ_{ax}	10.3	16.2	15.8



22

a) Chemical shifts were measured in C_6D_6 using TMS as an internal standard. Data for 1-adamantyl complex was taken from a reference (A. L. Balch, *J.Am.Chem. Soc.*, **1990**, 110, 7392)

b) Too broad to be detected at 23°C, but β_{eq} and β_{aq} protons appeared at -19.8 and -12.4 ppm at -25°C

Table 4-3. ^{1}H NMR Data of σ-(Alkyl)Fe^{III}(TPP) in C_6D_6 at 23°C.

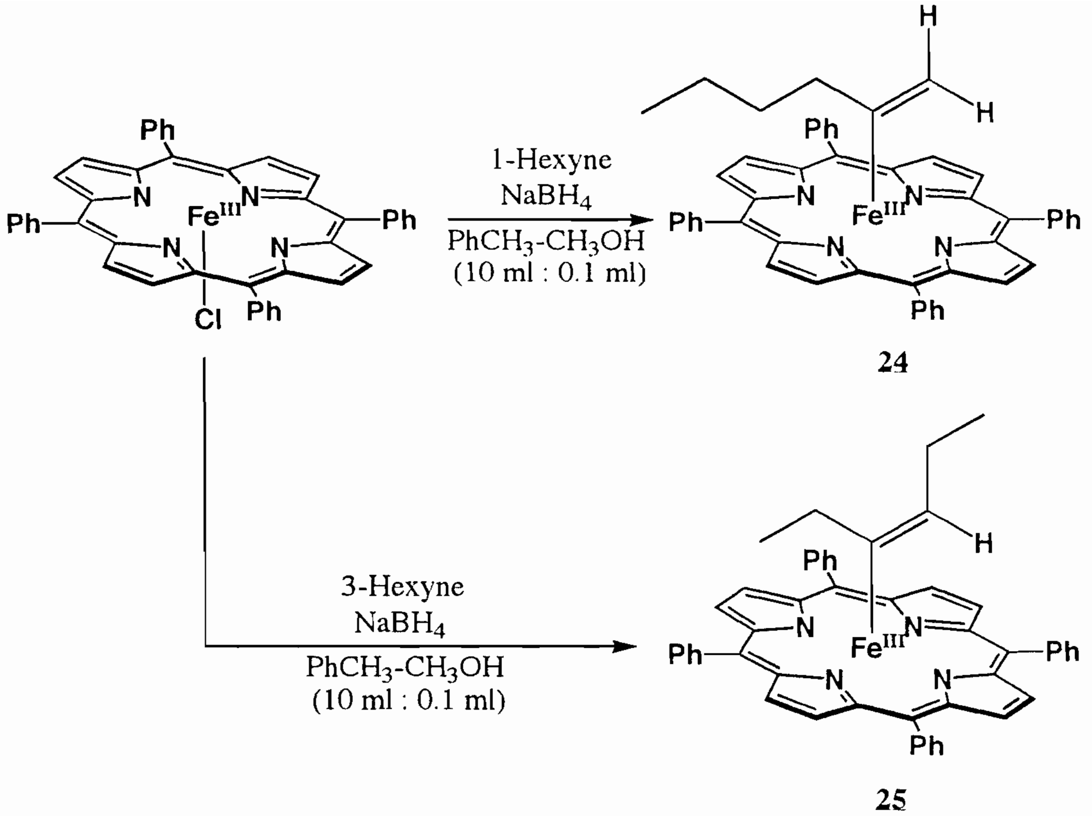
Complexes	Chemical shifts (δ-value from TMS)[a]							
	Porphyrin	Axial organo ligand						
	β-Pyrrole	β′-	α-	β-	γ-	δ-	ε-	ζ-
(17) σ-(Pentyl)(TPP)Fe^{III}-	-18.5(8H)	-	580(2H)	-63.5(2H)	18.4(2H)	11.9(2H)	n.d.	-
(18) σ-(1-Methylpropyl)(TPP)Fe^{III}	-17.54(4H)	-122(3H)	600(1H)	-85.2(1H)	29.2(1H)	7.9(3H)		-
	-17.50(4H)			-23.7(1H)	13.6(1H)			
(19) σ-(Hexyl)(TPP)Fe^{III}	-18.4(8H)	-	580(2H)	-60.8(2H)	18.7(2H)	12.2(2H)	n.d.	n.d.
(20) σ-(1-Methylbutyl)(TPP)Fe^{III}	-17.54(4H)	-120(3H)	600(2H)	-81.1(1H)	28.7(1H)	9.9(1H)	3.6(3H)	-
	-17.50(4H)			-25.6(1H)	14.2(1H)	8.7(1H)		
(28) σ-(1-Methylpentyl)(TPP)Fe^{III}	-17.56(4H)	-120(3H)	600(2H)	-79.1(1H)	29.1(1H)	9.9(1H)	5.1(1H)	3.2(3H)
	-17.50(4H)			-22.6(1H)	13.6(1H)	9.0(1H)	4.9(1H)	

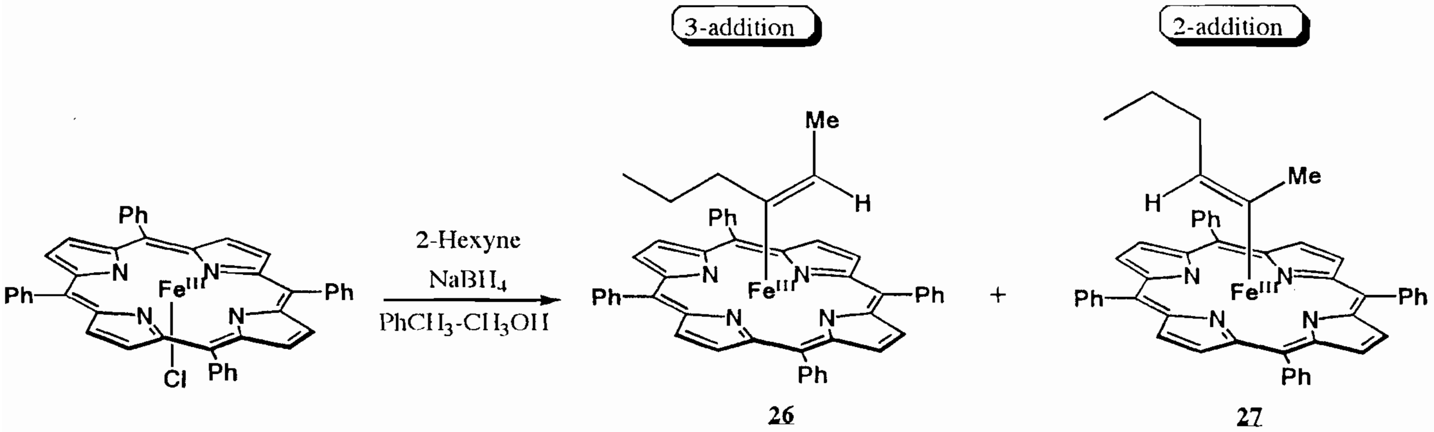
a) β′-, α-, β-, γ-, δ-, ε-, ζ-are positions relative to the metal center. ε- (for 17 and 19) and ζ-protons (for 19) were omitted as they could not be determined because of overlaping with aromatic protons or signals due to diamagnetic impurities. Signal multiplicity is singlet otherwise noted.

The ^{1}H-NMR signals due to the 3-methylcyclohexyl group of the complex **22** were assigned on the basis of the ^{1}H-NMR spectrum of the complex **21** as summarized in Table 4-2. In accord to the symmetric structure of **21**, the four broad resonances due to the β-protons were observed at -22.2, -23.3, -11.6 and -14.2 ppm at 23 °C. A set of three peaks at -35.0, 34.0 and 36.1 ppm were assigned to one γ-H_{eq} and two γ-H_{ax} protons. Thus, the γ-CH_3 groups is located at the *equatorial* position. This result with iron porphyrin is consistent with the finding that the thermodynamically most stable structure is generated in the hydrometallation of alkenes and alkynes with hydridocobalt porphyrins. A resonance peak of α-CH or α'-CH_2 was observed for the first time at around 600 ppm. The alternation of the spin of isotropic shifts upon going from α-CH to γ-CH signal is indicative of the spin polarization mechanism for the transmission of the spin on the iron to the axial organo ligand.

Reaction of (TPP)Fe^{III}Cl with Various Alkynes in the Presence of $NaBH_4$

(TPP)Fe^{III}Cl **1b** was treated with various alkynes, such as 1-hexyne, 2-hexyne, and 3-hexyne, and $NaBH_4$ in the mixture of toluene-methanol (10 ml: 0.2 ml) under argon at room temperature. The reaction was completed in a couple of minutes to give a red solution. The UV-Vis spectra of the reaction mixture of **1b** and 1-hexyne exhibits absorption maxima typical of σ-alkyliron(III)porphyrin at 410, 520 and 549 nm. Chromatographic separation on basic alumina with CH_2Cl_2 under argon afforded purple powders (91% yield) which showed a molecular ion due to $(C_6H_{11})Fe^{II}(TPP)$ (*m/z* 750) in the mass spectrum. The ^{1}H-NMR spectrum in degassed C_6D_6 solution showed signals due to a paramagnetic σ-type organoiron(III) porphyrin ($S=1/2$) along with a small amount of a diamagnetic iron porphyrin. The ^{1}H-NMR chemical shifts of these paramagnetic σ-type organoiron(III) porphyrin are a combination of the dipolar shift and the contact shift. The latter arises from delocalization of the spin into an orbital





	ratio	
	3-add.	2-add.
26 : **27**	1.9	1

$$\left(\frac{\Delta H}{H}\right)^{iso} = \left(\frac{\Delta H}{H}\right)^{dip} + \left(\frac{\Delta H}{H}\right)^{con}$$

$$\left(\frac{\Delta H}{H}\right)^{dip} = \frac{[\beta^2 s(s+1)(g^2_{//}-g^2_{\perp})(3\cos^2\theta-1)]}{9kTr^3}$$

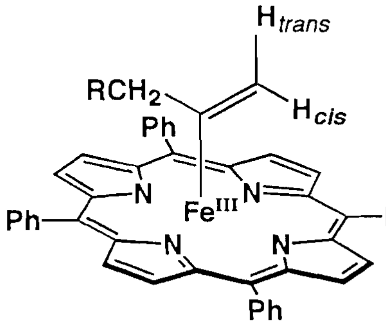
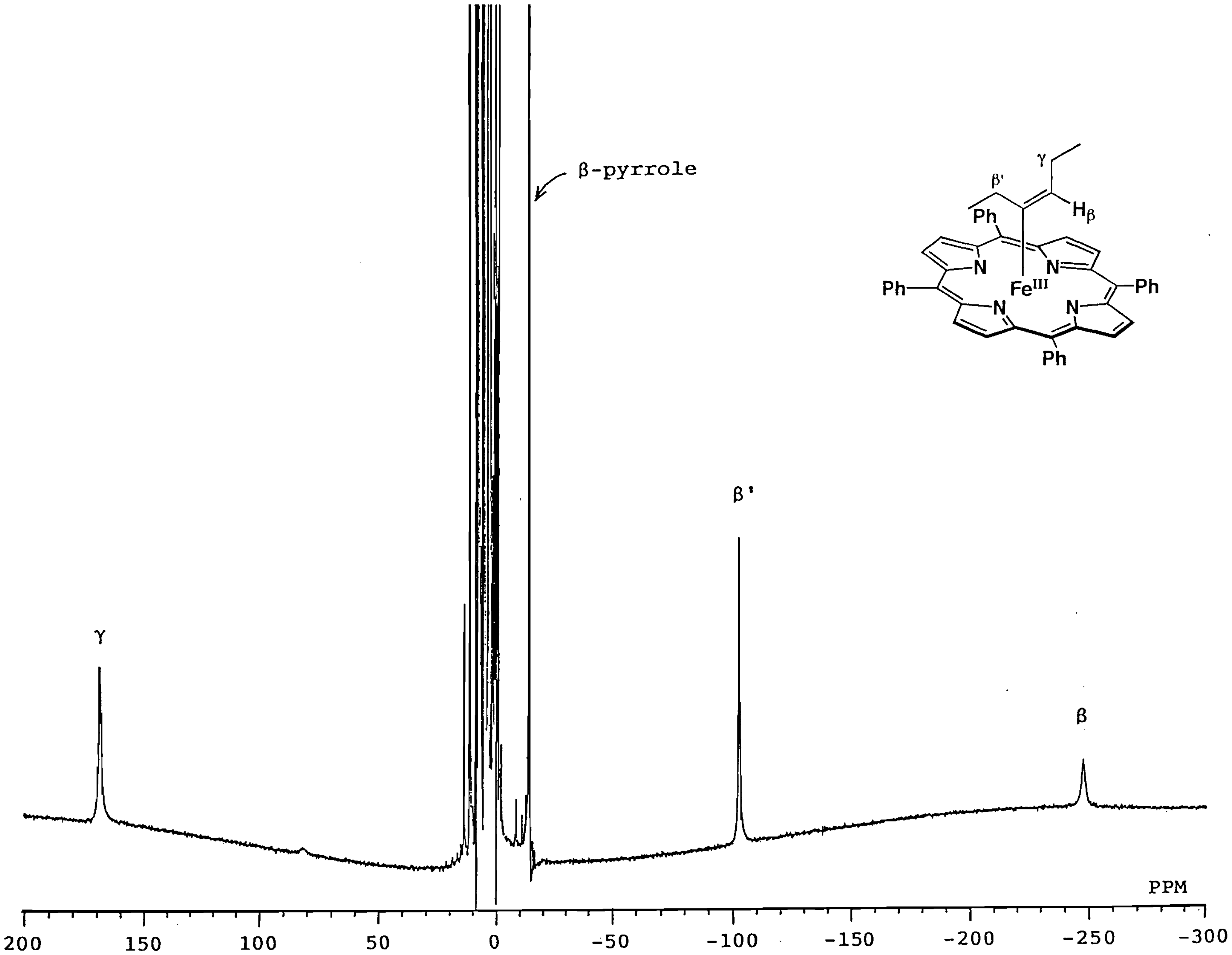


Table 4-4. Separation of Chemical Shifts into Contact and Dipolar Contributions for σ-(Vinyl)Fe^{III}(TPP) (benzene-d$_6$ at 23°C)

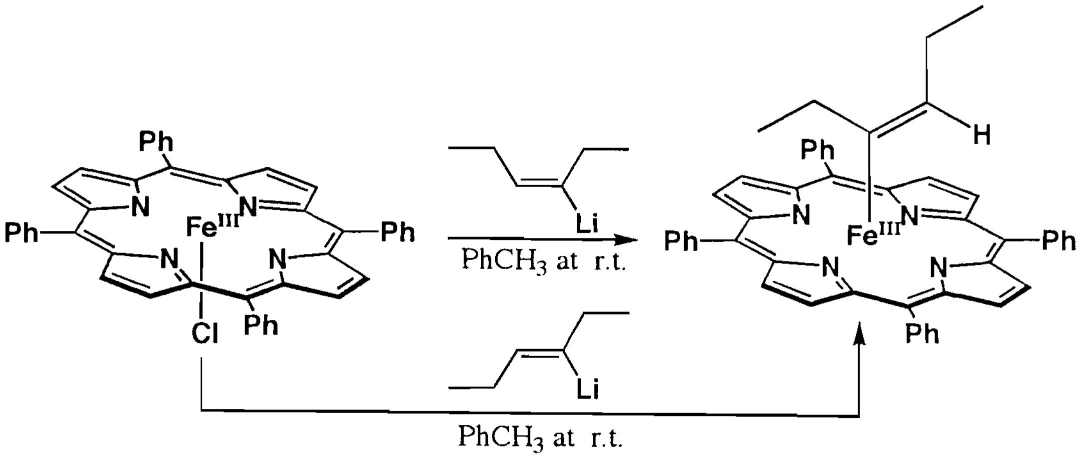
Protons	GF[a)]	$\left(\frac{\Delta H}{H}\right)^{ref.}$	$\left(\frac{\Delta H}{H}\right)^{ref.}$	$\left(\frac{\Delta H}{H}\right)^{iso.}$	$\left(\frac{\Delta H}{H}\right)^{dip.}$	$\left(\frac{\Delta H}{H}\right)^{con.}$
H_{trans}	$2.37\text{x}10^{-2}$	-333	-3.1	-329.9	40.4	-370.3
H_{cis}	$1.56\text{x}10^{-2}$	-192	-1.0	-191.0	26.6	-217.6

a) Relative geometric factors $(3\cos^2\theta-1)r^{-3}$ using Fe-C distans of 2.25Å

centered on the nucleus and the former arises from the through-space dipolar interaction with unpaired electrons. The dipolar shift is given by the following equation. Where θ is the angle between the iron-proton vector and the z axis, r is the length of this vector, T is absolute temperature and A is a constant. The contact shift is estimated by subtracting the dipole shift from the isotropic shift as shown in Table 4-4. Two vinyl protons of σ-(hex-1-en-2-yl)Fe^{III}(TPP) (**24**) were observed at -333 and -192 ppm. The dipolar contribution to H_{trans} and H_{cis} were estimated to be 40.4 and 26.6 ppm, respectively on the basis of the geometric factors and an ordinary coefficient for low spin iron(III) porphyrins (S=1/2). The contact terms for two vinyl protons were estimated to be (-370.3) and (-217.6) ppm as shown in table 4-4. Because the contact shift of H_{trans} is larger than that of H_{cis}


γ
β-pyrrole
β'
β
PPM
200
150
100
50
0
-50
-100
-150
-200
-250
-300
Ph
Ph
Ph
Ph
N
N
N
N
Fe^III
β'
γ
H_β

just like *vicinal* coupling constants in diamagnetic ^{1}H-NMR, the signal at -333 ppm is assigned to H_{trans} and that at -192 ppm is assigned to H_{cis}. The signal at -248 ppm is assigned to the vinyl proton of *E*-σ-(hex-3-en-3-yl)Fe^{III}(TPP) (**25**) on the basis of their intensity and line width. The *E*-configuration of **25** with respect to iron and β-alkyl group was determined by a comparison of two vinyl proton of **24** and **25**. *E* form. The signals at -103 and 169 ppm are assigned to the 2-CH_2, and 5-CH_2 protons of **25**, respectively, on the basis of their isotropic sifts, the major parts of which may be accounted for by the contact shifts due to σ-and π-transmission of the spin density of iron. The use of 2-hexyne in the above procedure afforded a mixture of two isomeric σ-(vinyl)Fe^{III}(TPP) derivatives, **26** and **27**. The ratio of the *E*-σ-(hex-2-en-3-yl)Fe^{III}(TPP)(**26**) and *E*-σ-(hex-2-en-2-yl)Fe^{III}(TPP) (**27**) was 1.9:1 on the basis of their ^{1}H-NMR signal intensities (see Table 4-5). The ^{1}H-NMR spectrum of **25** was identical with those of the organoiron(III) porphyrins synthesized by treating **1b** with organolithium reagents derived from *E*- and Z-(hex-3-en-3-yl)iodide.[9] This means that the stereochemical integrity of the corresponding (hex-3-en-3-yl)lithium reagents was lost during the reaction with **1b**. In fact, treatment of mixture of *E*- and *Z*-1-bromopropene (1:2.8 ratio) with lithium and then with **1b** in diethyl ether gave a mixture of *E*- and *Z*-σ-(prop-1-en-1-yl)Fe^{III}(TPP) isomers (**28**) and (**29**), in the ratio of 2.8:1 (ratio coincidentally reserved) based on ^{1}H-NMR analysis. The signals at -214 and -402 ppm of **28** and **29**, respectively, are associated with the *Z*- and *E*-β-vinyl protons, respectively, relative to iron on the basis of the fact that the contact shifts in the paramagnetic ^{1}H-NMR spectrum is roughly proportional to the spin coupling constant in the diamagnetic spectrum. The exclusive *cis*-addition of iron and hydrogen to 3-hexyne is in a remarkable contrast to the preferential *trans*-addition of cobalt and hydrogen. This suggests that a Fe(III)-C bond is more labile than a Co(III)-C bond to facilitate *E* to *E* isomerization to the more stable σ-vinyliron(III) porphyrins **25**.



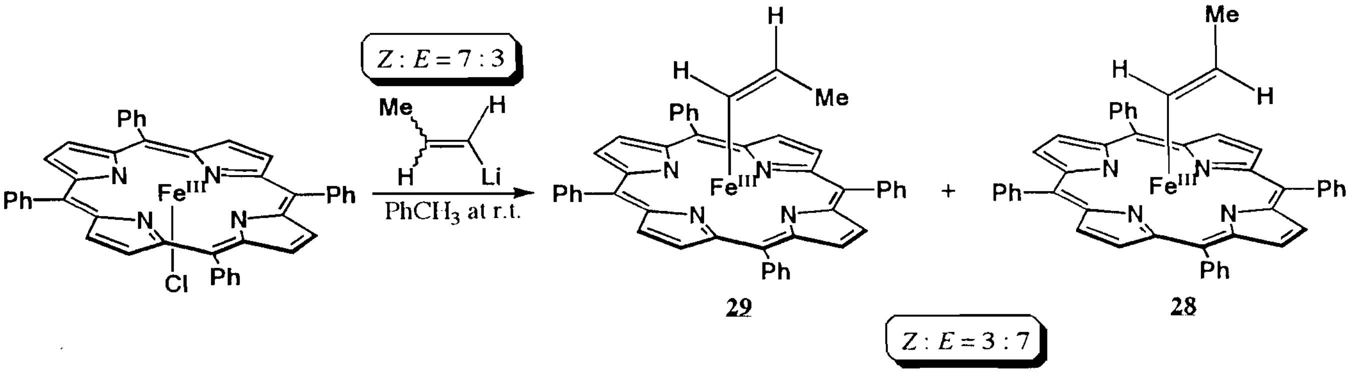


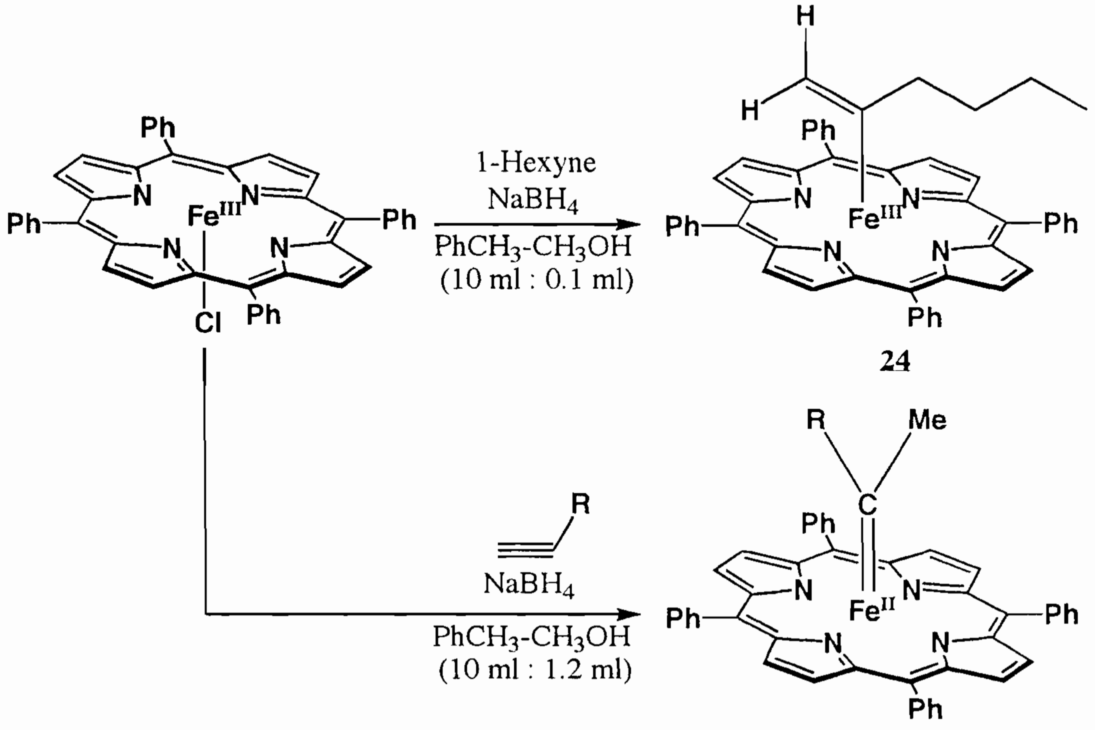
Table 4-5. ^{1}H NMR Data of σ-(Vinyl)Fe^{III}(TPP) in C_6D_6 at 23°C.

Complexes	Chemical shifts (δ-value from TMS)$^{a)}$							
	Porphyrin	Axial organo ligand						
	β-Pyrrole	γ'-	β'-	α-	β-	γ-	δ-	ε-
(24) σ-(Hex-1-en-2-yl)(TPP)Fe^{III}	-16.3(8H)	21.0(2H)	-64.2(2H)	-	-333(1H) -192(1H)	-	-	-
(25) (*E*)-σ-(Hex-3-en-3-yl)(TPP)Fe^{III}	-14.3(8H)	10.9(3H)	-103(2H)	-	-248(1H)	169(2H)	n.d.	-
(26) (*E*)-σ-(Hex-2-en-2-yl)(TPP)Fe^{III}	-14.3(8H)	-	-89.6(3H)	-	-253(1H)	189(2H)	n.d.	n.d.
(27) (*E*)-σ-(Hex-2-en-3-yl)(TPP)Fe^{III}	-14.3(8H)	n.d.	-103(2H)	-	-248(1H)	160(3H)	-	-
(28) (*Z*)-σ-(Prop-1-en-1-yl)(TPP)Fe^{III}	-16.3(8H)	-	-	229(1H)	-214(1H)	160(3H)	-	-
(29) (*E*)-σ-(Prop-1-en-1-yl)(TPP)Fe^{III}	-15.5(8H)	-	-	266(1H)	-402(1H)	127(3H)	-	-

a) γ'-, β'-, α-, β-, γ-, δ-, ε- are positions relative to the metal center. ε'- (for 24) and δ'-protons (for 24 and 26) were omitted as they could not be determined because of overlaping with aromatic protons or signals due to diamagnetic impurities. Signal multiplicity is singlet otherwise noted.

Reaction of (TPP)$Fe^{III}Cl$ with Terminal Alkynes in the Presence of $NaBH_4$ to Give Novel Dialkylcarbene Complexes

1b was also reacted with terminal alkynes (1-hexyne and 1-pentyne) and $NaBH_4$ in methanol rich conditions (toluene-methanol (4 ml:1.2 ml)) to give the diamagnetic iron porphyrins **30** and **31** after chromatographic purification on basic alumina under argon in 95 and 81% yields, respectively.



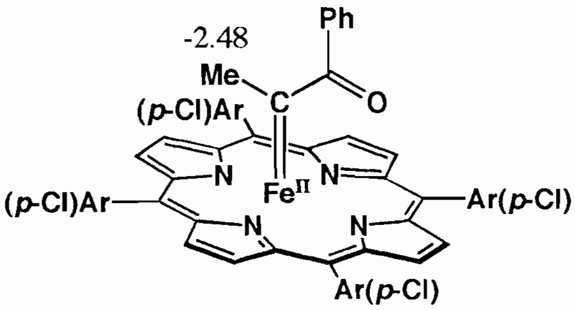
24

30 ; R=Bu
31 ; R=Pr

Table 4-7. The ^{1}H-NMR Spectral Data of **30** and **31** (in $CDCl_3$)

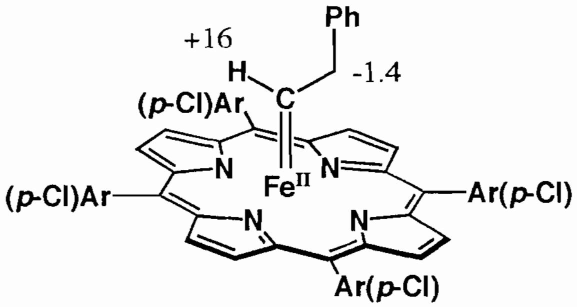
Compd.	Porphyrin	Axil organo ligand				
	β-Py	β'-	β-	γ-	δ-	ε-
1	8.68(s,8H)	-2.12(s,3H)	-1.62(t,2H)	-1.30(q,2H)	-0.21(se,2H)	0.11(t,3H)
2	8.68(s,8H)	-2.15(s,3H)	-1.72(t,2H)	-1.17(se,2H)	-0.21(t,2H)	

Table 4-7. ^{1}H-NMR and UV-Vis Data of Carbene Iron Porphyrins



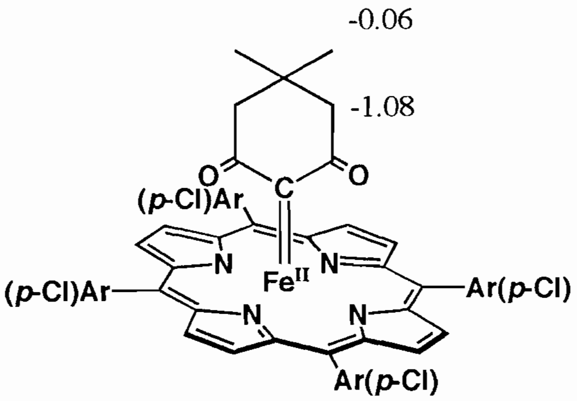
Solv.	CD_2Cl_2
Temp.	r.t.
UV-Vis	411
	520
	545

Mansuy
(1988)



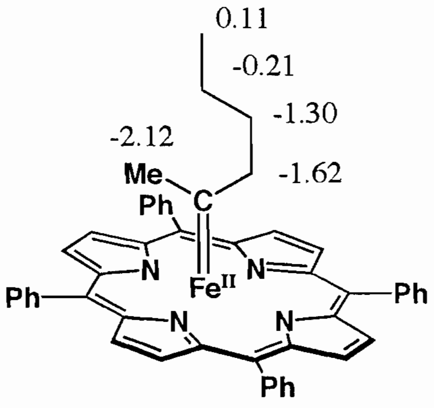
Solv.	CD_2Cl_2
Temp.	-10
UV-Vis	413
	519
	547

Mansuy
(1989)



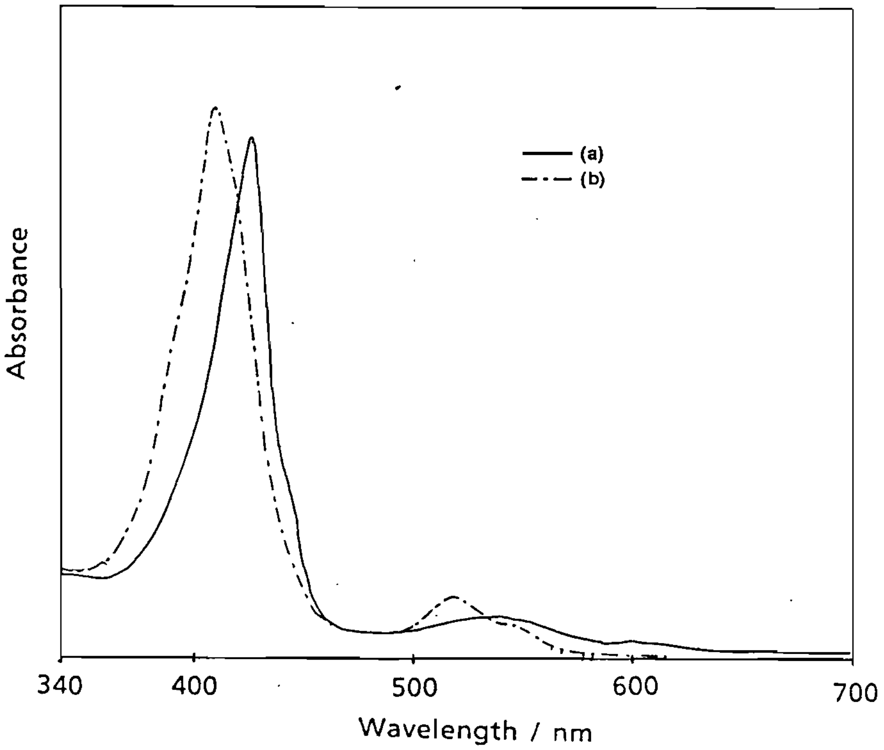
Solv.	CD_2Cl_2
Temp.	-40
UV-Vis	414
	512
	538

Mansuy
(1988)

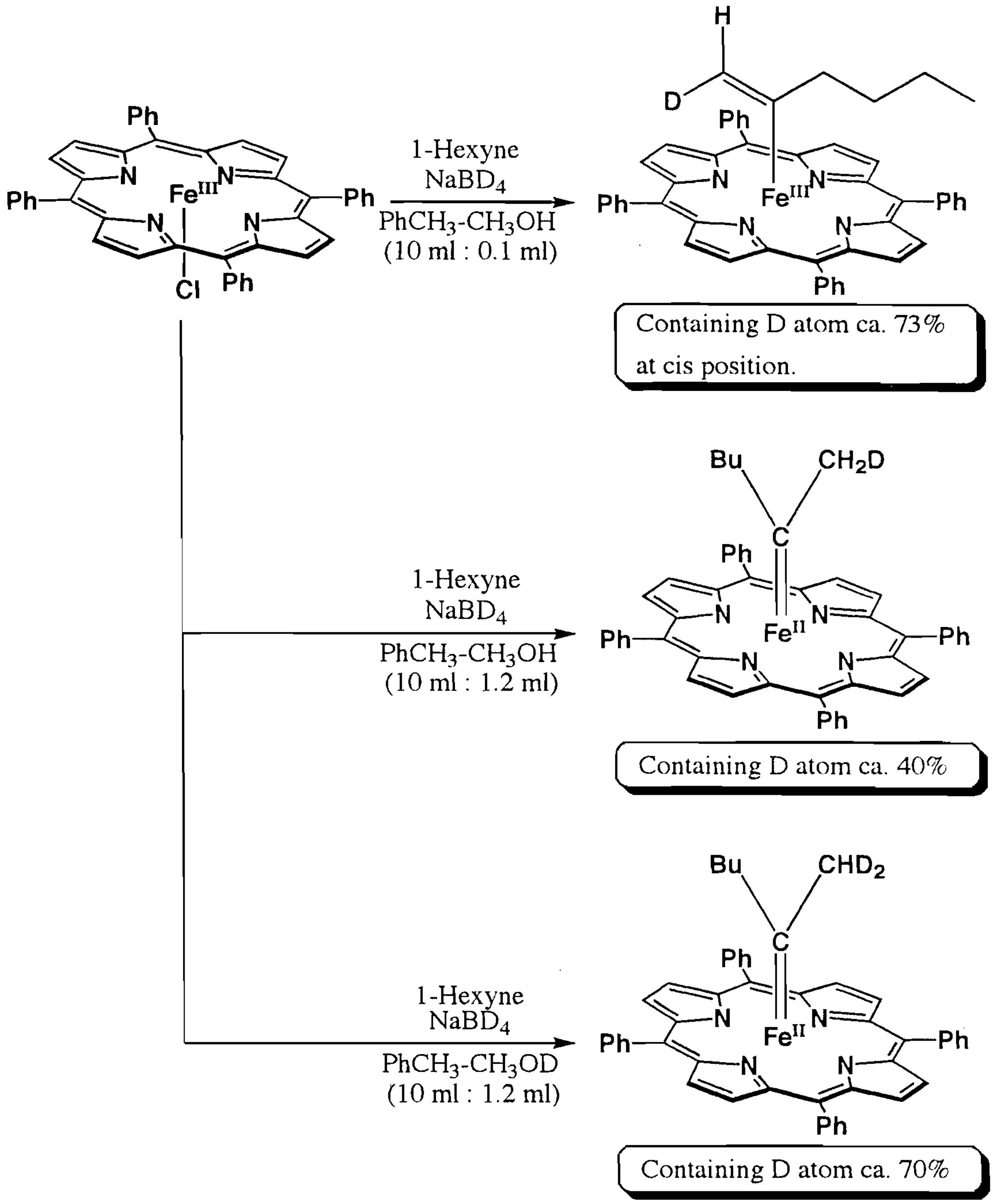


30

Solv.	C_6D_6
Temp.	r.t.
UV-Vis	410
	520
	546



The structure of compounds **30** and **31** was confirmed by the comparison with well characterized carbene iron(II) porphyrins as shown in Table 4-6. The UV-Vis spectra of **30** with absorptin maxima at 410, 520 and 549 nm were quite typical of organoiron(II) porphyrins. The ^{1}H-NMR spectra of **30** and **31** are similar to those of the carbeneiron(II) porphyrins reported by D. Mansuy as shown in Table 4-7. One singlet at about -2 ppm was assigned to the β'-methyl protons and signals at the region from -2 to 0.2 ppm were assigned to another alkyl protons. The C_{4v} symmetry of TPP ligand is confirmed by one singlet at 8.68 ppm due to β-pyrrole protons and signals in the region from 7 to 8 ppm due to *meso*-phenyl protons with 2:5 integration intensity. These diamagnetic ^{1}H-NMR spectra verify that (dialkylcarbene)Fe^{II} porphyrin was formed in this reaction. The mass spectrum of **30** showed a molecular ion due to $(C_6H_{12})Fe^{II}(TPP)$ (*m/z* 751). Peaks due to $Fe^{II}(TPP)$ (*m/z* 667: M - 84 and 668: M - 83) and to $(C_6H_{12})_2Fe^{II}(TPP)$ (*m/z* 835: M + 84) were also observed. This disproportionation in the mass spectrum is frequently noted in carbene complexes of metalloporphyrins. These spectroscopic data of **30** and **31** are consistent with a dialkylcarbene complex, (methylbutylcarbene)Fe^{II}(TPP) and (methylpropylcarbene)Fe^{II}(TPP), respectively. Although a large number of (carbene)Fe^{II} porphyrins have been prepared by Mansuy from polyhalogenated compounds or diazo compounds, **30** and **31** are the first examples of dialkylcarbene complexes of Fe^{II} porphyrins.



Containing D atom ca. 73% at cis position.

Containing D atom ca. 40%

Containing D atom ca. 70%

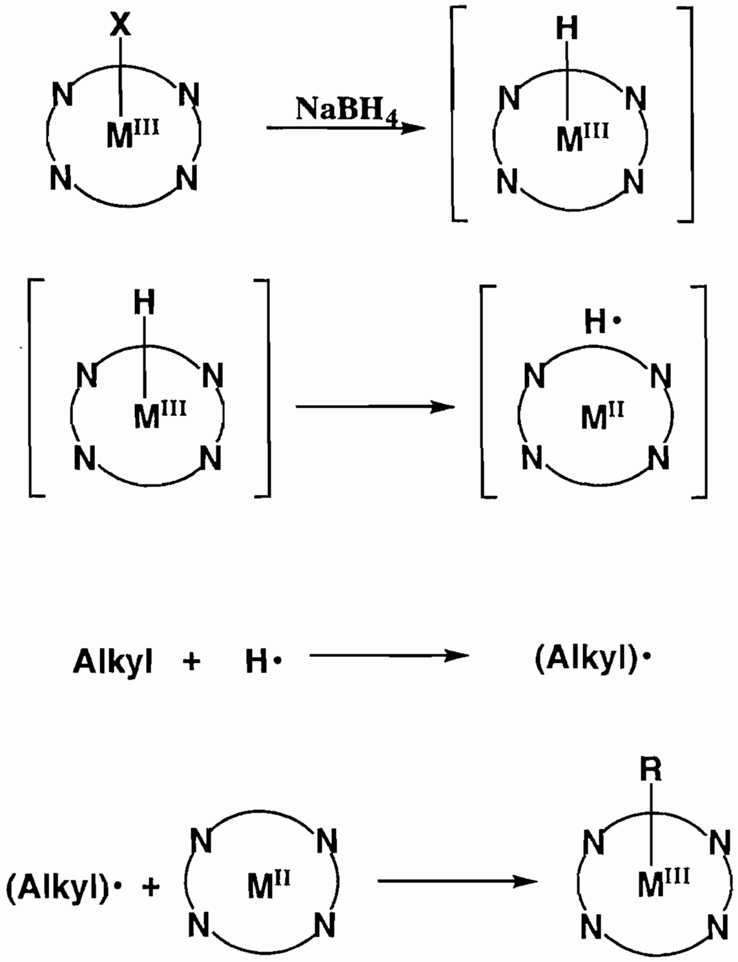
When **1b** was allowed to react with 1-hexyne and $NaBH_4$ in toluene-methanol (4 ml : 0.1 ml), a considerable amount of the σ-(vinyl)Fe^{III} complex **24** was formed along with **30**. The experiments under various reaction conditions were performed to understand this reaction mechanism. The results are summarized in Scheme 4-1. When $NaBD_4$, 1-hexyne, C_7H_8 and CH_3OH were employed, approximately one-third of the β-methyl protons of **30** was deuteriated (^2H content 40% by ^1H-NMR). Whereas two-thirds of the β-methyl protons of **30** was deuteriated (^2H content 70% by ^1H-NMR) when $NaBD_4$ 1-hexyne, C_7H_8 and CH_3OD were employed.

Reaction Mechanism

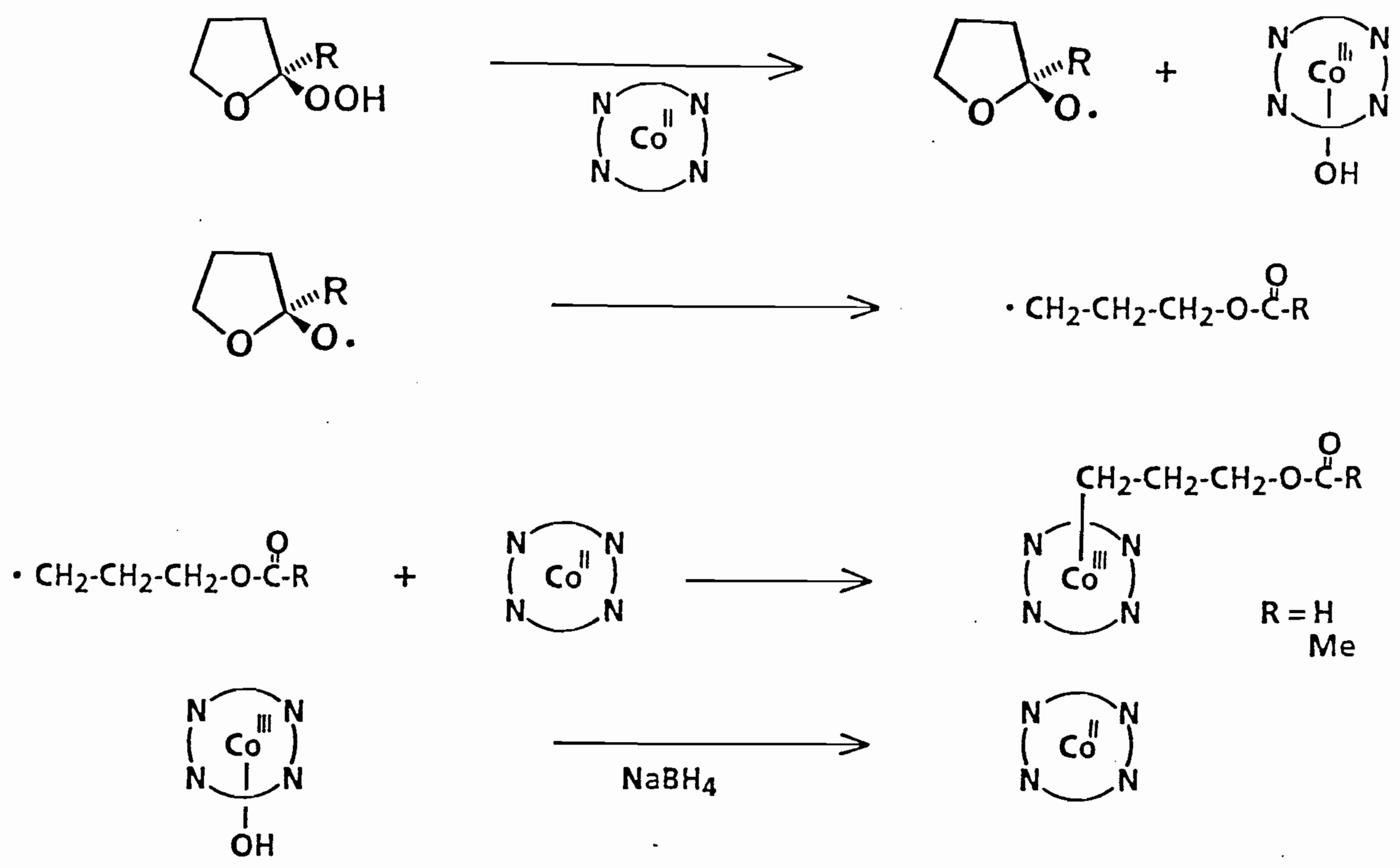
A proposed reaction mechanism of the hydrometallation of alkyne and alkene by the use of $NaBH_4$ is exhibited in Scheme 4-1. Hydridometal(III) porphyrins are generated from the reaction of metal(III) porphyrins with BH_4^- ion. A hydrogen radical which is generated from metal-hydrogen bond homolysis combines with substrates to form thermodynamically most stable radical intermediates. These intermediates are trapped by nearby divalent metal porphyrins to afford σ-vinyl or σ-alkyl metal(III) complexes. Metal(II) porphyrins play a key role not only by participating in the formation of hydrogen radical, as a so called initiator, but also by capturing vinyl or alkyl radicals, as a so called trapping reagent. In the case of cobalt(II) porphyrin, a cobalt(II) porphyrin is oxidized to the corresponding cobalt(III) porphyrin by a limited amount of oxygen. Indeed, the reaction of (OEP)Co^{III}Cl with 1-hexyne gave a σ-vinyl complex in a low yield. But reoxidation of Co^{II} to Co^{III} *in situ* led to excellent yields of organocobalt(III) porphyrins not only because a hydridocobalt(III) intermediate is regenerated in the presence of excess $NaBH_4$ but also organocobalt(III) porphyrin is stable against oxygen. Hydridometal(III) porphyrins would undergo bimolecular H_2 elimination as is known for rhodium and ruthenium porphyrins. But the hydrometallation is much faster than the bimolecular H_2 elimination of hydride-metal(III) porphyrin. The stereo- and regioselectivity in the hydrometallation of alkenes and alkynes with metal porphyrins is basically determined by the stability of the organic radicals (alkyl: tertiary > secondary > primary; vinyl: *trans* > *cis*) generated through the addition of hydrogen radical to alkenes and alkynes. However, a tertiary alkyl radical or a congested secondary alkyl radical can not make a stable M^{III}-C bond due to the steric repulsion with a porphyrin ligand. Thus σ-(1-ethylalkyl)Fe^{III}(TPP) complex which should take place in the reaction of 2- and 3-alkenes could not be observed but rearrangement via β-elimination-addition sequence of a Fe^{III}-H bond with a C-C double bond gave σ-(1-methylalkyl)Fe^{III}(TPP) complexes.

While radical-like cobalt(II) porphyrin decomposes peroxide to give a *tert*-butoxy radical which was responsible for hydrogen abstraction from the α-position of THF and tetrahydropyran. At present we can not conclude whether the hydrogen abstraction from THF and THP is caused by this hydrogen radical or the *tert*-butoxy radical. Tetrahydrofuran 2-hydroperoxide would be similarly decomposed by **1a** to afford alkoxy radicals which can undergo carbon-carbon bond cleavage to give γ-acyloxypropyl radicals or carbon-oxygen bond cleavage to give acylalkoxy radicals. The latter would lead to cationic cobalt(III) complexes while the former would give σ-(alkyl)cobalt(III) complexes.

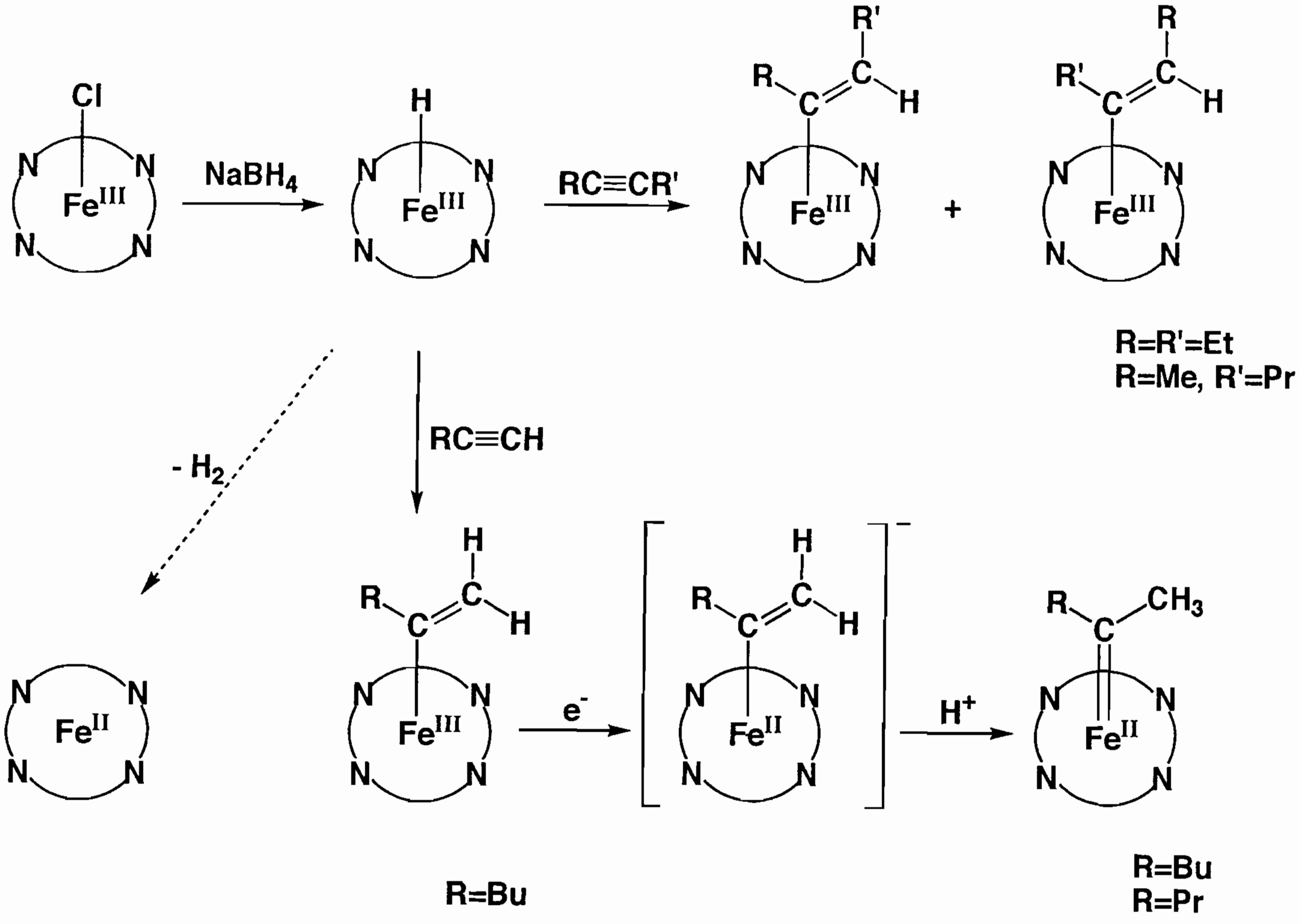
A proposed reaction mechanism of the formation of dialkylcarbene complexes is exhibited in Scheme 4-3. This mechanism is consistent with the observation that approximately one-third of the β-methyl protons of **30** was deuteriated (^{2}H content 40% by ^{1}H-NMR) when $NaBD_4$ 1-hexyne, C_7H_8 and CH_3OH were employed, whereas two-third of the β-methyl protons of **30** was deuteriated (^{2}H content 70% by ^{1}H-NMR) when $NaBD_4$ 1-hexyne, C_7H_8 and CH_3OD were employed. The intermediacy of the anionic σ-(vinyl)Fe^{II}(TPP) in the conversion of **25** to **31** seems reasonable, since it has been shown that such anionic σ-(vinyl)Fe^{II} porphyrins are formed *via* electrochemical reduction (-0.6 V *vs.* standard calomel electrode) of σ-(vinyl)Fe^{III} porphyrins. Actually, anionic σ-alkyl iron(II) porphyrin complexes are recently synthesized and fully characterized by A. L. Balch.[10] This suggests that terminal alkynes undergo regioselective hydrometallation to give a σ-(alk-1-en-2-yl)Fe^{III} complex which is subsequently reduced and protonated under the reaction conditions. It is also well known that carbeneiron(II) porphyrin is a key intermediates in the reduced metabolism of organo halogeno compounds by cytochlome P-450. In this chapter I revealed that alkynes gave dialkylcarbene complexes under the strongly reducting conditons. While cobalt and rhodium porphyrins have so far been shown to catalyze monooxygenation of a limited number of alkenes in the presence of $NaBH_4$ and O_2, we have unambiguously demonstrated that **1a** reacts not only with a wide range of alkenes but also with alkyl ethers to give organocobalt(III) complexes under similar reaction conditions. In particular, the latter reaction is regarded as the first example of C-H activation by Co^{II} related to alkane hydroxylation in the cytochrome P-450 chemistry.



Scheme 4-1 Reaction Mechanism



Scheme 4-2 Reaction Mechanism



Scheme 4-3 Reaction Mechanism

Experimental Section

General Comments; ^{1}H-NMR including 2D-Cosy spectra were recorded in deuteriochloroform by using a JEOL GX-270 spectrometer (270-MHz), and chemical shifts are referenced to tetramethylsilane. Coupling constants of pyrrolic and aromatic protons are in a normal range (about 5 and 8 Hz, respectively) and will not be specified. UV-Vis spectra were taken in dichloromethane solution on a Shimadzu UV-240 or a Shimadzu-UV-245Fs spectro-meter. IR spectra measurements were made in a KBr disk with a Shimadzu IR-420 spectrometer. Elemental Analyses were performed on a Yanaco CHN MT2 recorder using acetanilide as a standard compound. OEPCo^{II} was prepared by a literature procedure[7]. THF was distilled from sodium benzophenone ketyl under argon atmosphere.

Hydrometallation of Alkynes and Alkenes

General Procedure; OEPCo(II) (**1a**) (ca. 50 mg) and excess amount of $NaBH_4$ (ca. 30 eq.) were placed in a two-necked flask fitted with a sealed rubber septum and a three-way stop-cock which was joined to a vacuum pump and a balloon. When the atmosphere was replaced with argon, benzene (ca. 12 ml) and methanol (ca. 0.4 ml) were added with syringe via a sealed rubber septum, and then excess amount (ca. 30 eq.) of substrates were added with a syringe by way of a sealed rubber septum. **1a** was completely dissolved after stirring for 12 hours in the dark condition. The reaction mixture was evaporated and the residue was dissolved in benzene in order to remove unreacted cobalt(II) porphyrin and $NaBH_4$ (twice). Recrystallization from CH_2Cl_2-methanol gave novel σ-cobalt(III) complexes.

σ-(β-styryl)Co^{III}(OEP) 2; The reaction was performed by using phenyl acetylene. According to the general procedure, compound **2** was obtained in 59% yield: ^{1}H-NMR δ($CDCl_3$) 10.05 (singlet, 4H, *meso*-H), 4.01 (doublet of quartet, 16H, CH_2CH_3), 1.87 (triplet, 24H, CH_2CH_3), 4.76 (doublet of doublet, 2H, *o*-Ph), 5.70 (triplet, 2H, *m*-Ph), 6.28 (triplet, 1H, *p*-Ph), -2.67, -0.83 (doublet, 1Hx2, vinyl-H, $J_{vicinal}$=2.2 Hz); UV-Vis(CH_2Cl_2) λ_{max} 393, 553; Anal. Calcd for $C_{44}H_{51}N_4CoH_2O$: C,76.05; H,7.40; N,8.48. Found. C,74.19; H,7.40; N,8.00.

σ-(hex-1-en-2-yl)Co^{III}(OEP) 3; The reaction was performed by using 1-hexyne. According to the general procedure, compound **2a** was obtained in 73% yield.: ^{1}H-NMR δ($CDCl_3$) 10.08 (singlet, 4H, *meso*-H), 1.87 (triplet, 24H, CH_2CH_3), 4.01 (doublet of quartet, 16H, CH_2CH_3), -3.12, -0.96 (doublet of doublets, doublet, 1Hx2, vinyl-H, $J_{vicinal}$=3.57 Hz,J_{allyl}=1.99 Hz), -4.29 (triplet, 2H, 3-CH_2), -1.75 (quartet, 2H, 4-CH_2), -0.66 (sextet, 2H, 5-CH_2), -0.23 (triplet, 3H, 6-CH_3); UV-Vis(CH_2Cl_2) λ_{max} 395, 552; Anal. Calcd for $C_{42}H_{55}N_4CoH_2O$: C,76.06; H,8.21; N,8.30. Found. C,67.01; H,8.45; N,7.18.

(*Z*)-σ-(hex-3-en-3-yl)(OEP)Co^{III} 4a and **(*E*)-σ-(hex-3-en-3-yl)(OEP)Co^{III} 4b**; The reaction was performed by using 3-hexyne. According to the general procedure, compound **4a** and **4b** were obtained as a mixture in 33% total yield:**4a** ^{1}H-NMR δ($CDCl_3$) 9.86 (singlet, 4H, *meso*-H), 1.84 (triplet, 24H, CH_2CH_3), 3.95 (doublet of quartet, 16H, CH_2CH_3), -0.80 (triplet, 1H, 4-CH), -1.77 (triplet, 3H, 1-CH_3), -4.42 (quartet, 2H, 2-CH_2), -3.02 (quintet, 2H, 5-CH_2), -1.05 (triplet, 3H, 6-CH_3) **4b**; ^{1}H-NMR δ($CDCl_3$) 10.04 (singlet, 4H, *meso*-H), 1.84 (triplet, 24H, CH_2CH_3), 3.95 (doublet of quartet, 16H, CH_2CH_3), -3.58 (triplet, 1H, 4-CH), -0.96 (triplet, 3H, 1-CH_3), -0.20 (quartet, 2H, 2-CH_2), -2.61 (triplet, 3H, 6-CH_3). The 3-CH_2 protons could not be determined because of overlaping with other signals

(*Z*)-σ-(hex-2-en-2-yl)Co^{III}(OEP) 5a, (*E*)-σ-(hex-2-en-2-yl)Co^{III}(OEP) 5b, (*Z*)-σ-(hex-2-en-3-yl)Co^{III}(OEP) 6a and **(*E*)-σ-(hex-2-en-3-yl)Co^{III}(OEP) 6b**; The reaction was performed by using 2-hexyne. According to the general procedure, compound 5a, **5b**, **6a** and **6b** were obtained as a mixture in 31% total yield;

σ-(1-Methylbutyl)Co^{III}(OEP) 7 (Method A); The reaction was performed by using 1-hexene. According to the general procedure, compound 7 was obtained in 83% yield: ^{1}H-NMR δ($CDCl_3$) 10.28 (singlet, 4H, *meso*-H), 1.86 (triplet, 24H, CH_2CH_3), 4.00 (doublet of quartet, 16H, CH_2CH_3), -5.88 (doublet, 3H, 1-CH_3), -3.95 (broad, 1H, 2-CH), -6.04, -4.61 (multipletx2, 1Hx2, 3-CH_2), -1.52, -1.28 (multipletx2, 1Hx2, 4-CH_2), -0.71, -0.61 (multipletx2, 1Hx2, 5-CH_2), -0.32 (triplet, 3H, 6-CH_3); UV-Vis(CH_2Cl_2) λ_{max} 391, 516, 552; Anal. Calcd for $C_{42}H_{57}N_4CoH_2O$: C,72.39; H,8.53; N,8.04. Found. C,72.43; H,8.10; N,8.43.

σ-(1-Methylbutyl)Co^{III}(OEP) 7 (Method B); 1-Hexene (ca. 30 eq.) was added to suspension of (OEP)Co^{II} (ca. 50 mg) in CH_2Cl_2 (50 ml). The solution was stirred for about 15 minutes under an aerobic atmosphere to almost complete dissolution. The reaction mixture was evaporated and the residue was dissolved in benzene in order to remove unreacted cobalt(II) porphyrin and $NaBH_4$ (twice). Recrystallization from CH_2Cl_2-methanol gave 7 in 84% yield. Spectral data are shown above.

σ-(1-Methylpropyl)Co^{III}(OEP) 8; The reaction was performed by using 2-pentene. According to the general procedure, compound **8** was obtained in 68% yield: ^{1}H-NMR δ($CDCl_3$) 9.98 (singlet, 4H, meso-H), 1.85 (triplet, 24H, CH_2CH_3), 3.99 (doublet of quartet, 16H, CH_2CH_3), -5.72 (doublet, 3H, 1-CH_3), -3.95 (broad, 1H, 2-CH), -6.17, -4.54 (multipletx2, 1Hx2, 3-CH_2), -1.55, -1.29 (multipletx2, 1Hx2, 4-CH_2), -1.00 (triplet, 3H, 5-CH_3); UV-Vis(CH_2Cl_2) λ_{max} 391, 515, 545; Anal. Calcd for $C_{41}H_{55}N_4Co \cdot 3H_2O$: C,68.69; H,8.58; N,7.82. Found. C,68.85; H,8.50; N,7.39.

σ-(cyclopentyl)Co^{III}(OEP) 9; The reaction was performed by using cyclopentene which was pre-treated with active aluminum oxide. According to the general procedure, compound **10** was obtained in 89% yield: ^{1}H-NMR δ($CDCl_3$) 10.03 (singlet, 4H, *meso*-H), 1.87(triplet, 24H, CH_2CH_3), 3.99 (doublet of quartet, 16H, CH_2CH_3), -3.8 (broad, 1H, α-CH), -6.13, -4.11 (multiplet, 2Hx2, β-CH_2), -1.28, -0.94 (multiplet, 2Hx2, γ-CH_2); UV-Vis(CH_2Cl_2) λ_{max} 391, 516, 551; Anal. Calcd for $C_{41}H_{53}N_4CoH_2O$: C,72.34; H,8.17; N,8.25. Found. C,72.65; H,8.16; N,8.46.

σ-(cyclohexyl)Co^{III}(OEP) 10; The reaction was performed by using cyclohexene which was pre-treated with active aluminum oxide. According to the general procedure, compound **10** was obtained in 74% yield: ^{1}H-NMR δ($CDCl_3$) 10.05 (singlet, 4H, *meso*-H), 1.89 (triplet, 24H, CH_2CH_3), 3.99 (doublet of quartet, 16H, CH_2CH_3), -3.8 (broad, 1H, α-CH), -5.1, -4.8 (multipletx2, 2Hx2, β-CH_2), -1.2, -1.0 (multipletx2, 2Hx2, γ-CH_2), -0.9, -0.3 (multipletx2, 1Hx2, δ-CH_2),; UV-Vis(CH_2Cl_2) λ_{max} 391, 516, 551; Anal. Calcd for $C_{42}H_{55}N_4CoH_2O$: C,72.81; H,8.29; N,8.09. Found. C,73.11; H,8.31; N,8.08.

σ-(3-tetrahydrofuranyl)Co^{III}(OEP) 11; OEPCo(II) (1a) (ca. 50 mg) and excess amount of $NaBH_4$ (ca. 30 eq.) were placed in a two-necked flask fitted with a sealed rubber septum and a three-way stop-cock which was joined to a vacuum pump and a balloon. When the atmosphere was replaced with argon, 2,5-dihydrofuran which was pre-treated with active aluminum oxide was added with a syringe via a sealed rubber septum. **1a** was completely dissolved after stirring for 12 hours in the dark. The reaction mixture was evaporated. The residue was dissolved in benzene the cobalt(II) porphyrin and $NaBH_4$ were filtered off twice. Recrystallization from CH_2Cl_2-methanol gave compound **11** in 91% yield: ^{1}H-NMR δ($CDCl_3$) 10.12 (singlet, 4H, *meso*-H), 1.87 (triplet, 24H, CH_2CH_3), 4.02 (doublet of quartet, 16H, CH_2CH_3), -4.13 (broad, 1H, 3-CH), -3.78, -1.81 (multipletx2, 1Hx2, 2-CH_2), -5.80, -3.60 (multipletx2, 1Hx2, 4-CH_2), 1.18x2 (multipletx2, 1Hx2, 5-CH_2); ^{13}C-NMR δ($CDCl_3$) 90.0 (*meso*-C), 143.3 (α,β-pyrrole-C), 18.5, 19.9 (CH_2CH_3), 28.6 (4-$\underline{C}H_2$), 68.5 (2-$\underline{C}H_2$), 59.3 (6-$\underline{C}H_2$); UV-Vis(CH_2Cl_2) λ_{max} 390, 517, 551; Anal. Calcd for $C_{41}H_{53}N_4CoH_2O$: C,72.34; H,8.17; N,8.25. Found. C,72.65; H,8.16; N,8.46.

σ-(2-tetrahydrofuranyl)Co^{III}(OEP) 12; The reaction was performed by using 2,3-dihydrofuran which was pre-treated with active aluminum oxide. According to the above procedure, compound **11** and **12** were obtained as a mixture in 87% total yield.

Reaction of Cobalt(II) Porphyrin, Ethers and Sodium Tetrahydroborate in the Absence or Presence of tert-Buthylhydroperoxides

σ-(2-tetrahydrofuranyl)Co^{III}(OEP) 12; OEPCo(II) (**1a**) (ca. 50 mg) and excess amount of $NaBH_4$ were placed in a two-necked flask fitted with a sealed rubber septum and a three-way stop-cock which was joined to a vacuum pump and a balloon. When the atmosphere was replaced with argon, tetrahydrofuran distilled from sodium benzophenone ketyl under argon was added with a syringe via a sealed rubber septum. **1a** was completely dissolved after stirring for 12 hours in the dark. The reaction mixture was evaporated. The residue was dissolved in benzene the cobalt(II) porphyrin and $NaBH_4$ were filtered off twice. Recrystallization from CH_2Cl_2-methanol gave compound **12** in 75% yield: ^{1}H-NMR δ($CDCl_3$) 10.00 (singlet, 4H, *meso*-H), 1.85 (triplet, 24H, CH_2CH_3), 4.00 (doublet of quartet, 16H, CH_2CH_3), -1.99 (broad, 1H, 2-CH), -4.95, -3.97 (multipletx2, 1Hx2, 3-CH_2), -2.83, -0.78 (multipletx2, 1Hx2, 4-CH_2), -0.79, 0.85 (multipletx2, 1Hx2, 5-CH_2); ^{13}C-NMR δ($CDCl_3$) 98.4 (*meso*-C), 142.3, 143.3 (α,β-pyrrole-C), 18.5, 19.3 (CH_2CH_3), 31.4 (4-CH_2), 28.8 (3-CH_2), 67.0 (5-CH_2); UV-Vis(CH_2Cl_2) λ_{max} 391, 516, 551; Anal. Calcd for $C_{41}H_{53}N_4CoH_2O$: C,72.34; H,8.17; N,8.25. Found. C,72.65; H,8.16; N,8.46.

σ-(2-tetrahydropyranyl)Co^{III}(OEP) 13; OEPCo(II) (**1a**) (ca. 50 mg) and excess amount of $NaBH_4$ were placed in a two-necked flask fitted with a sealed rubber septum and a three-way stop-cock which was joined to a vacuum pump and a balloon. When the atmosphere was replaced with argon and tetrahydropyran which was treated with active aluminum oxide was added with syringe via a sealed rubber septum. Then, *tert*-butylhydroperoxide was added with a syringe by way of a sealed rubber septum. **1a** was completely dissolved after stirring for ten minutes in the dark. The reaction mixture was evaporated. The residue was dissolved in benzene in order to remove of unreacted cobalt(II) porphyrin and $NaBH_4$ (twice), and recrystallization from CH_2Cl_2-methanol gave compound **13** in 75% yield: ^{1}H-NMR δ($CDCl_3$) 10.03 (singlet, 4H, *meso*-H), 1.84 (triplet, 24H, CH_2CH_3), 3.99 (doublet of quartet, 16H, CH_2CH_3), -3.05 (broad, 1H, 2-CH), -5.27, -4.72 (multipletx2, 1Hx2, 3-CH_2), -2.82, -1.57 (multipletx2, 1Hx2, 4-CH_2), -0.98, -0.49 (multipletx2, 1Hx2, 5-CH_2), -0.49, 0.92 (multipletx2, 1Hx2, 6-CH_2); UV-Vis(CH_2Cl_2) λ_{max} 391, 516, 550; Anal. Calcd for $C_{42}H_{55}N_4Co$: C,74.75; H,8.21; N,8.30. Found. C,73.88; H,8.55; N,8.30.

Reaction of Cobalt(III) Porphyrin, Allylic Substrates and Sodium Tetrahydrobran in the Presence of *t*-Butylhydroperoxide

σ-(1-Methylbutyl)Co^{III}(OEP) 7; 1-Hexene was added to the suspension of (OEP)Co^{II} (ca. 50 mg) in benzene-methanol (40 ml:5 ml). After t-butylhydroperoxide was added, the solution was stirred for about 15 minutes to almost complete dissolution. The reaction mixture was evaporated and the residue was dissolved in benzene in order to remove unreacted cobalt(II) porphyrin and $NaBH_4$ (twice). Recrystallization from CH_2Cl_2-methanol gave **7** in 66% yield. Spectral data are shown before.

σ-(1-Methyl-2-phenylethyl)Co^{III}(OEP) 14; To suspension of (OEP)Co^{II} (ca. 50 mg) in benzene-methanol (40 ml: 5 ml) was added allylbenzene and t-butylhydroperoxide and the solution was stirred for about 15 minutes to almost complete dissolution. The reaction mixture was evaporated and the residue was dissolved in benzene in order to remove unreacted cobalt(II) porphyrin and $NaBH_4$ (twice). Recrystallization from CH_2Cl_2-methanol gave **14** in 74% yield: ^{1}H-NMR δ($CDCl_3$) 10.04 (singlet, 4H, *meso*-H), 1.86 (triplet, 24H, CH_2CH_3), 4.00 (doublet of quartet, 16H, CH_2CH_3), -5.72 (doublet, 3H, 1-CH_3), -4.12 (broad, 1H, 2-CH), -4.97, -3.19 (doublet of doublet, triplet, 1Hx2, 3-CH_2), 4.66 (doublet, 1Hx2, *o*-Ph), 6.27 (triplet, 1Hx2, *m*-Ph), 6.42 (triplet, 1H, *p*-Ph); UV-Vis(CH_2Cl_2) λ_{max} 391, 518, 550; Anal. Calcd for $C_{45}H_{55}N_4Co$: C,76.03; H,7.80; N,7.88. Found. C,71.06; H,7.03; N,8.75.

Reactions of Cobalt(II) Porphyrins with Various Hydroperoxides

σ-(γ-formoxypropyl)Co^{III}(OEP) 15; OEPCo^{II} (ca. 50 mg) and excess amount of $NaBH_4$ were placed in a two-necked flask fitted with a sealed rubber septum and a three-way stop-cock which was joined to a vacuum pump and a balloon. When the atmosphere was replaced with argon, aged tetrahydrofuran which contains α-hydroperoxide was added with a syringe via a sealed rubber septum. After stirring for 12 hours in the dark, the unreacted cobalt(II) porphyrin and $NaBH_4$ were removed by precipitation with benzene twice. Recrystallization from CH_2Cl_2-methanol gave compound **15** in 93% yield: ^{1}H-NMR δ($CDCl_3$) 10.06 (singlet, 4H, *meso*-H), 1.87 (triplet, 24H, CH_2CH_3), 4.01 (doublet of quartet, 16H, $C\underline{H}_2CH_3$), -4.37 (triplet, 2H, α-$C\underline{H}_2$), -4.93 (quintet, 2H, β-$C\underline{H}_2$), 0.91 (triplet, 2H, γ-$C\underline{H}_2$), 6.58 (singlet, 1H, -OC$\underline{H}$O); ^{13}C-NMR δ($CDCl_3$) 98.5 (*meso*-C), 143.0, 143.3 (α,β-pyrrole-C), 18.4, 19.9 (CH_2CH_3), 26.9 (β-$\underline{C}H_2$), 57.4 (γ-$\underline{C}H_2$), 159.3 (O$\underline{C}$HO); IR (KBr) 1700, 1730 cm^{-1}; UV-Vis(CH_2Cl_2) λ_{max} 390, 517, 550; Anal. Calcd for $C_{40}H_{51}N_4O_2CoH_2O$: C,68.95; H,7.67; N,8.04. Found. C,68.60; H,7.37; N,7.97.

σ-(γ-acetoxypropyl)Co^{III}(OEP) 16; The reaction was performed by using 2-methyltetrahydrofuran pretreated with 10 % KOH aqueous solution in order to remove an anti-oxidant, aerated for two weeks, and stored over molecular sieves. According to the general procedure, compound **16** was obtained in 50% yield: ^{1}H-NMR δ($CDCl_3$) 10.05 (singlet, 4H, *meso*-H), 1.87 (triplet, 24H, CH_2CH_3), 3.99 (doublet of quartet, 16H, CH_2CH_3), -4.35 (triplet, 2H, α-CH_2), -4.93 (quintet, 2H, β-CH_2), 0.85 (triplet, 2H, γ-CH_2), 1.18 (singlet, 3H, -$OCOCH_3$); UV-Vis(CH_2Cl_2) λ_{max} 391, 516, 550; Anal. Calcd for $C_{41}H_{58}N_4O_2CoH_2O$: C,69.28; H,7.80; N,7.88. Found. C,69.81; H,7.59; N,7.98.

Alternative Syntheses of 9 and 16

General Procedure; OEPCo(II) (**1a**) (ca. 100 mg) and sodium amalgam (25%, ca. 3.0 g) were placed in a three-necked flask fitted with a sealed rubber septum, connected with a vacuum pump, and jointed with a two-necked flask fitted with a sealed rubber septum. When the atmosphere was replaced with argon, tetrahydrofuran distilled from sodium benzophenone ketyl under argon was added with a syringe via a sealed rubber septum. The color of the solution changed from reddish purple to lustrous orange-red. After the solution was transferred to the two-necked flask, an excess amount of degassed alkyl halide (ca. 30 eq.) was added with a syringe by way of a sealed rubber septum. The solution was stirred for ten minutes in the dark. The color of the solution changed to dark red. CH_2Cl_2 was added to the reaction mixture and the solution was then poured into 200 ml of ice-water. The organic layer was separated, successively washed with water (200 mlx3), and dried over Na_2SO_4. The organic layer was evaporated and the residue was dissolved in benzene in order to remove unreacted cobalt(II) porphyrin and $NaBH_4$ (twice). Recrystallization from CH_2Cl_2-methanol gave novel σ-cobalt(III) complexes.

σ-(cyclopentyl)Co^{III}(OEP) 9; The reaction was performed by using bromocyclopentene. According to the general procedure, compound **9** was obtained in 35% yield. Spectral data are shown before.

σ-(γ-acetoxypropyl)Co^{III}(OEP) 16; The reaction was performed by using 1-bromoacetoxypropyl. According to the general procedure, compound **16** was obtained in 42% yield. Spectral data are shown before.

Synthesis of σ-Alkyl, σ-Vinyl and Dialkylcarbene Iron(III) Porphyrins

General Procedure; (TPP)$Fe^{III}Cl$ (**1b**) (ca. 15 mg) was placed in two necked flask fitted with a sealed rubber septum and a two-way atop-cock which was jointed to a vacuum pump and covered with a sheet of aluminum tin. When the atomosphere was replaced with argon twice, the mixture of degassed toluene-methanol-substrate was added via a sealed rubber septum. The color of the reaction mixture changed from brown to red in a few minutes. Then the solvent was completely removed under vacuum for a period of several hours. The residue was extracted with a degassed d_6 benzene and purified by quickly passing through a short column of basic alumina under argon atomosphere and then the degassed d_6 benzene of the organoiron porphyrins was placed in a NMR tube, capped with a rubber septum, and sealed with parafilm. In a typical experiment, the sample was immediately analyzed by ^1H-NMR spectroscopy.

σ-(pentyl)Fe^{III}(TPP) 17; The reaction was performed by using toluene-methanol-1-pentene (10 ml : 0.2 ml : 1 ml). According to the general procedure, a mixture of compound **17** and **18** was analyzed by ^1H-NMR spectroscopy. **17;** ^1H-NMR $\delta(C_6D_6)$ -18.5 (singlet, 8H, β-pyrrole), 580 (broad singlet, 2H, α-CH_2), -63.5 (singlet, 2H, β-CH_2), 18.4 (singlet, 2H, γ-CH_2), 11.9 (singlet, 2H, δ-CH_2), The ε-CH_3 protons could not be determined because of overlaping with aromatic protons or signals due to diamagnetic impurities.

σ-(1-Methylpropyl)Fe^{III}(TPP) 18; The reaction was performed by using toluene-methanol-2-pentene (10 ml : 0.2 ml : 1 ml). According to the general procedure, compound **18** was immediately analyzed by ^1H-NMR spectroscopy: ^1H-NMR $\delta(C_6D_6)$ -17.81, -17.90 (singletx2, 4Hx2, β-pyrrole), -122 (singlet, 3H, β'-CH_3), 600 (broad singlet, 1H, α-CH), -85.2, -23.7 (singletx2, 1Hx2, β-CH_2), 29.2, 13.6 (singletx2, 1Hx2, γ-CH_2), 7.9 (singlet, 3H, δ-CH_3)

σ-(hexyl)Fe^{III}(TPP) 19; The reaction was performed by using toluene-methanol-2-hexene (10 ml : 0.2 ml : 1 ml). According to the general procedure, a mixture of compound **19** and **20** was analyzed by ^{1}H-NMR spectroscopy. **19**; ^{1}H-NMR δ(C_6D_6) -18.4 (singlet, 8H, β-pyrrole), 580 (broad singlet, 2H, α-CH_2), -60.8 (singlet, 2H, β-CH_2), 18.7 (singlet, 2H, γ-CH_2), 12.2 (singlet, 2H, δ-CH_2), The ε-CH_2 and ζ-CH_3 protons could not be determined because of overlaping with aromatic protons or signals due to diamagnetic impurities.

σ-(1-Methylbutyl)Fe^{III}(TPP) 20; The reaction was performed by using toluene-methanol-2-hexene(10 ml : 0.2 ml : 1 ml). According to the general procedure, compound **20** was immediately analyzed by ^{1}H-NMR spectroscopy: ^{1}H-NMR δ(C_6D_6) -17.50, -17.54 (singletx2, 4Hx2, β-pyrrole), -120 (singlet, 3H, β'-CH_3), 600 (broad singlet, 1H, α-CH), -81.1, -25.6 (singletx2, 1Hx2, β-CH_2), 28.7, 14.2 (singletx2, 1Hx2, γ-CH_2), 8.7, 9.9 (singletx2, 1Hx2, δ-CH_2), 3.6 (singlet, 3H, ε-CH_3)

σ-(cyclohexyl)Fe^{III}(TPP) 21; The reaction was performed by using toluene-methanol-cyclohexene (10 ml : 0.2 ml : 1 ml). According to the general procedure, compound **21** was analyzed by ^{1}H-NMR spectroscopy: ^{1}H-NMR δ(C_6D_6) -18.3 (singlet, 8H, β-pyrrole), -20.8 (singlet, 1Hx2, β_{eq}-CH), 600 (broad singlet, 1H, α-CH), -30.4 (singlet, 1Hx2, γ_{eq}-CH), 34.1 (singlet, 1Hx2, γ_{ax}-CH), -12.8 (singlet, 1H, δ_{eq}-CH), 16.2 (singlet, 1H, δ_{ax}-CH) The β_{ax}-CH protons signal could not be detected at 23 °C, but the β_{eq}-CH and β_{ax}-CH protons appeared at -19.8 and -12.4 ppm at -25 °C.

σ-(3-Methylcyclohexyl)Fe^{III}(TPP) 22; The reaction was performed by using toluene-methanol-3-methylcyclohexene (10 ml : 0.2 ml : 1 ml). According to the general procedure, compound **22** was immediately analyzed by ^{1}H-NMR spectroscopy: ^{1}H-NMR δ(C_6D_6) -18.2 (singlet, 8H, β-pyrrole), -22.2, -223.4 (singletx2, 1Hx2, β_{eq}-CH), 14.2, -11.8 (singlet, 1Hx2 β_{ax}-CH), 600 (broad singlet, 1H, α-CH), -35.0, (singlet, 1H, γ_{eq}-CH), 34.0, 36.1 (singletx2, 1Hx2, γ_{ax}-CH), -10.3 (singlet, 1H, δ_{eq}-CH), 15.8 (singlet, 1H, δ_{ax}-CH), The γ-CH_3 protons could not be determined because of overlaping with aromatic protons or signals due to diamagnetic impurities.

σ-(1-methylpentyl)Fe^{III}(TPP) 23; The reaction was performed by using toluene-methanol-3-heptene (10 ml : 0.2 ml : 1 ml). According to the general procedure, compound **23** was immediately analyzed by ^{1}H-NMR spectroscopy: ^{1}H-NMR δ(C_6D_6) -17.50, -17.56 (singletx2, 4Hx2, β-pyrrole), -120 (singlet, 3H, β'-CH_3), 600 (singlet, 1H, α-CH), -79.1, -22.6 (singletx2, 1Hx2, β-CH_2), 29.1, 13.6 (singletx2, 1Hx2, γ-CH_2), 9.9, 9.0 (singletx2, 1Hx2, δ-CH_2), 5.1, 4.9 (singletx2, 1Hx2, ε-CH_2), 3.2 (singlet, 3H, ζ-CH_3)

σ-(hex-1-en-2-yl)Fe^{III}(TPP) 24; (TPP)Fe^{III}Cl (**1b**) (ca. 50 mg) was placed in two necked flask fitted with a sealed rubber septum and a two-way atop-cock which was jointed to a vacuum pump and covered with a sheet of aluminum tin. When the atomosphere was replaced with argon twice, the mixture of degassed toluene-methanol-1-hexyne (10 ml : 0.1 ml : 1 ml) was added via a sealed rubber septum. The color of the reaction mixture changed from brown to red in a few minutes. Then the solvent was completely removed under vacuum for a period of several hours. The residue was extracted with a degassed dichloromethane and purified by quickly passing through a column of basic alumina under argon atomosphere. Then the solvent was completely removed under vacuum for a period of several hours. The yeild of compound **24** was 81%: ^{1}H-NMR δ(C_6D_6) -16.3 (singlet, 8H, β-pyrrole), -333, -192 (singletx2, 1Hx2, vinyl-H), -64.2 (singlet, 2H, β'-CH_2), 21.0 (singlet, 2H, γ'-CH_2); UV-Vis(CH_2Cl_2) λ_{max} 410, 520, 549

(*E*)-σ-(hex-3-en-3-yl)Fe^{III}(TPP) 25 ; The reaction was performed by using toluene-methanol-3-hexyne (10 ml : 0.2 ml : 1 ml). According to the general procedure, compound **25** was analyzed by ^{1}H-NMR spectroscopy: ^{1}H-NMR δ(C_6D_6) -14.3 (singlet, 8H, β-pyrrole), -248 (singlet, 1H, vinyl-H), -103 (singlet, 2H, β'-CH_2), 169 (singlet, 2H, γ-CH_2), 10.9 (singlet, 3H, γ-CH_3), The δ-CH_3 protons could not be determined because of overlaping with aromatic protons or signals due to diamagnetic impurities.

(*E*)-σ-(hex-2-en-2-yl)Fe^{III}(TPP) 26 and **(*E*)-σ-(hex-2-en-3-yl)Fe^{III}(TPP) 27;** The reaction was performed by using toluene-methanol-3-hexyne (10 ml : 0.2 ml : 1 ml). According to the general procedure, a mixture of compound **26** and **27** was analyzed by ^{1}H-NMR spectroscopy. **26;** ^{1}H-NMR δ(C_6D_6) -14.3 (singlet, 8H, β-pyrrole), -103 (singlet, 2H, β'-CH_2), -248 (singlet, 1H, β-CH), 160 (singlet, 3H, γ-CH_3), The γ-CH_2 and δ-CH_3 protons signals could not be detected to other overlap signals. **27;** ^{1}H-NMR δ(C_6D_6) -14.3 (singlet, 8H, β-pyrrole), -89.6 (singlet, 3H, β'-CH_3), -253 (singlet, 1H, β-CH), 189 (singlet, 2H, γ-CH_2), The δ-CH_2 and ε-CH_3 protons could not be determined because of overlapping with aromatic protons or signals due to diamagnetic impurities.

(*Z*)-σ-(prop-1-en-1-yl)Fe^{III}(TPP) 28 and **(*E*)-σ-(prop-1-en-1-yl)Fe^{III}(TPP) 29;** **1a** (ca. 20 mg) was placed in a two-necked flask fitted with a sealed rubber septum and connected with a vacuum pump. When the atmosphere was replaced with argon, toluene distilled from sodium benzophenone ketyl under argon was added with a syringe via a sealed rubber septum. A reagent which was treated a mixture of *E*- and Z-1-bromopropene (1 : 2.8 ratio) with lithium (ca. 1.3 eq.) was added with a syringe by way of a sealed rubber septum. The solution was stirred for a few minutes in the dark. The color of the solution changed to red. Then the solvent was completely removed under vacuum. The residue was extracted with a degassed dichloromethane and purified by quickly passing through a column of basic alumina under argon atomosphere. Then the solvent was completely removed under vacuum for a period of several hours. Then a mixture of compound **28** and **29** was analyzed by ^{1}H-NMR spectroscopy. **28;** ^{1}H-NMR δ(C_6D_6) -16.3 (singlet, 8H, β-pyrrole), 229 (singlet, 2H, α-CH), -214 (singlet, 1H, β-CH), 160 (singlet, 3H, γ-CH_3) **29;** ^{1}H-NMR δ(C_6D_6) -15.5 (singlet, 8H, β-pyrrole), 266 (singlet, 1H, α-CH), -402 (singlet, 1H, β-CH), 127 (singlet, 3H, γ-CH_3)

σ-(Methylbutylcarbene)Fe^{II}(TPP) 30; (TPP)Fe^{III}Cl (**1b**) (ca. 50 mg) was placed in two necked flask fitted with a sealed rubber septum and a two-way atop-cock which was jointed to a vacuum pump and covered with a sheet of aluminum tin. When the atomosphere was replaced with argon twice, the mixture of degassed toluene-methanol-1-hexyne (10 ml : 1.2 ml : 1 ml) was added via a sealed rubber septum. The color of the reaction mixture changed from brown to red in a few minutes. Then the solvent was completely removed under vacuum for a period of several hours. The residue was extracted with a degassed dichloromethane and purified by quickly passing through a column of basic alumina under argon atomosphere. Then the solvent was completely removed under vacuum for a period of several hours. The yeild of compound **30** was 95%: ^{1}H-NMR δ(C_6D_6) 8.68 (singlet, 8H, β-pyrrole), -2.12 (inglet, 3H, β'-CH_3), -1.62 (triplet, 2H, β-CH_2), -1.30 (quintet, 2H, γ-CH_2), -0.21 (sextet, 2H, δ-CH_2), 0.11 (triplet, 3H, ε-CH_3); UV-Vis(CH_2Cl_2) λ_{max} 410, 520, 549; mass m/z 751

σ-(Methylpentylcarbene)Fe^{II}(TPP) 31; The reaction was performed by using toluene-methanol-1-pentyne (10 ml : 1.2 ml : 1 ml). According to the above procedure, the yeild of compound **31** was 81%: ^{1}H-NMR δ(C_6D_6) 8.68 (singlet, 8H, β-pyrrole), -2.15 (singlet, 3H, β'-CH_3), -1.72 (triplet, 2H, β-CH_2), -1.17 (quintet, 2H, γ-CH_2), -0.21 (triplet, 3H, δ-CH_3)

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881

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