Pure & Appl. Chem., Vol. 68, No. 1, pp. 1-8, 1996.
Printed in Great Britain.

Transition metal complexes as bifunctional carriers of polar organometallics: Their application to large molecule modifications and to hydrocarbon activation

Carlo Floriani

Institut de Chimie Minérale et Analytique, Université de Lausanne, BCH 3307,
CH-1015 Lausanne, Switzerland

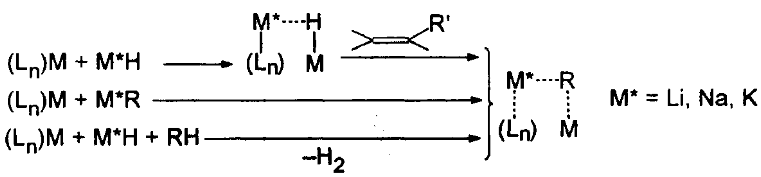
Abstract: Modifications of the *meso*-octaethylporphyrinogen have been successful using a bifunctional approach in the application of organometallic methodologies. The homologation of *meso*-octaethylporphyrinogen to *meso*-octaethyltris(pyrrole)monopyridine and to *meso*-octaethylbis(pyrrole)bispyridine were carried out by reacting carbon monoxide with Zr-C and Zr-H functionalities respectively, supported by the auxiliary ligand *meso*-octaethylporphyrinogen, [$Et_8N_4H_4$]. Such an homologation of a pyrrole to a pyridine ring within the porphyrinogen skeleton was achieved with high selectivity, controlled regiochemistry, good yield and on multiple gram quantities. A novel mode of electrophilic activation of aliphatic C-H bonds, assisted by zirconium(IV) in conjunction with an excess of MH [M = Li, Na, K], allows the metalation and then functionalization of the *meso*-octaethylporphyrinogen periphery. Reaction of σ bond metathesis allowed the isomerization of zirconium-alkyl functionalities and the activation of aliphatic hydrocarbons.

1. Introduction

The major aim of this lecture is to emphasize some conceptual approaches to the modification of organic substrates using organometallic chemistry. The keyword in this context is "bifunctionality". Bifunctional coordination compounds have as part of their structure two complementary reactive sites which assist an organic substrate transformation. Such bifunctional compounds display the ability to carry polar functionalities, which are exemplified by alkali metal organometallics, and to assist their trasformations. For example, organocuprates (1) act as carriers of lithium organometallics and exhibit a bifunctional nature, expressed by the intervention of both lithium and copper during the reactions. Such characteristics are rarely found in other organometallic reagents (2).

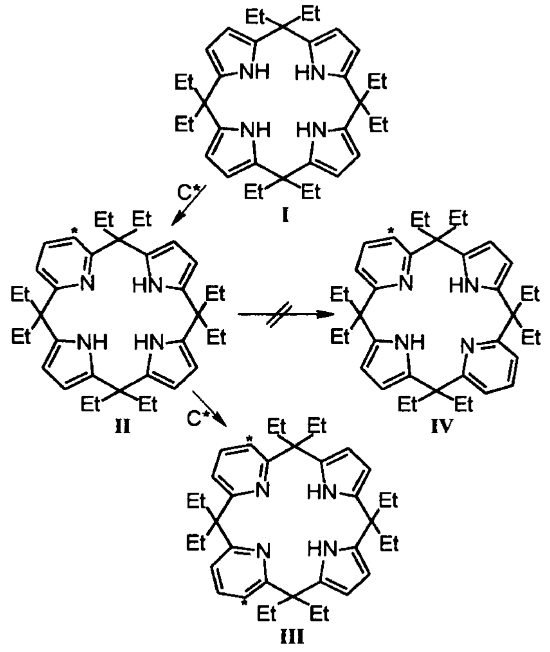
The bifunctional approach involves a lithium alkyl or a Grignard reagent being 'carried' by a transition metal and as a result with alterated reactivity. The generation of such bimetallic organic functionalities is exemplified in Scheme 1, where the ligand environment of M, L_n, has appropriate basic sites for binding the alkali cation.

SCHEME 1. Bifunctional Polar Organometallic Carriers

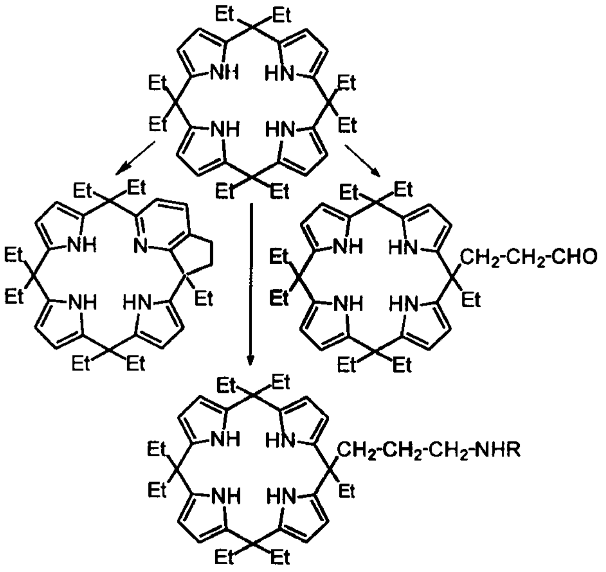


We used the *meso*-octaethylporphyrinogen [$Et_8N_4H_4$], **1** (3), as the auxiliary ligand, L_n, in these bifunctional complexes (4-9), with the added advantage that it could also act as the "organic substrate". The choice of such a target molecule is particularly relevant to the chemistry of "artificial porphyrins" formed from *meso*-octaethylporphyrinogens *via* non-conventional oxidation pathways (6). In this context, modification of the porphyrinogen skeleton may shed more light on the mechanism of this transformation. Traditionally, such modifications of the porphyrinogen skeleton could be achieved using conventional organic assembling methods but we will approach this problem using organometallic methodologies. We will focus on two different reactions. First, the homologation of a pyrrole to a pyridine ring. This is particularly interesting as it has led to a novel class of modified porphyrinogens (7) with altered metal binding and redox properties (Scheme 2) to those of the parent compound. Second, the functionalization of one or two out of the eight peripheral aliphatic chains (Scheme 3) (8).

SCHEME 2. Homologation of porphyrinogen skeleton



SCHEME 3. Side chain functionalization of porphyrinogen



2. Bifunctional metal-porphyrinogen complexes

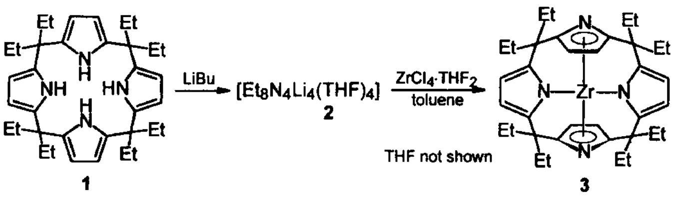
The binding of *meso*-octaethylporphyrinogen to a transition metal has been achieved via the intermediacy of the fully deprotonated form available as a tetralithium derivative only. Its structure and superbase properties have been recently described in detail (9). Compounds derived from the porphyrinogen metal complexation show some peculiar properties:

i) the bifunctional nature of early transition metal complexes, where the central metal acts as a Lewis acid and the electron-rich periphery can bind, for instance, alkali cations, allows one to use them as bifunctional carriers of polar organometallics (4-6);

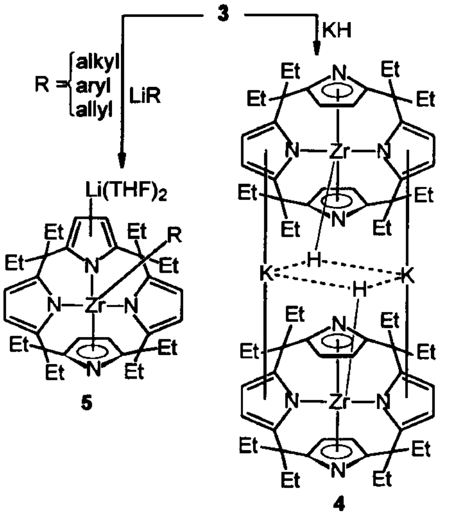
ii) the four pyrrolyl anions, due to the conformational flexibility assured by the *meso* sp^3 carbons, can adapt their bonding mode (η^1, η^3, or η^5) to the electronic requests of the metal (Scheme 4) (5);

iii) the three-dimensional structure of the ligand engenders a protected cavity for very reactive species formed on the metal (6,7).

SCHEME 4.



SCHEME 5.



The Zr-H and Zr-C functionalities play a primary role in the development of organometallic chemistry and in the application of organometallic methodologies to organic synthesis and catalysis (10). In addition, an equally important role is played by the alkali-organometallics (11). The use of zirconium-*meso*-octaalkylporphyrinogen complexes as carriers for polar organometallics (5,7,8) will take advantage of both approaches and eventually represents a move towards the use of such complexes as catalysts. We report here a number of examples of polar organometallics, involving alkalis, particularly potassium, carried by the zirconium-*meso*-octaethylporphyrinogen complex, **3** (5,7,8). These potassium derivatives can add as such, or can be formed directly on the carrier *via* a hydrozirconation reaction (12) or metathesis from another alkali derivative. Formation of bimetallic zirconium-alkali-hydrido and zirconium-alkali-alkyl complexes are shown in Scheme 5.

The bimetallic alkyls have been obtained either from the reaction of **3** with the corresponding alkali organometallics, or via the hydrozirconation reaction requiring the addition of olefins to the dimeric zirconium-alkali hydride like **4**. The reaction between **3** and alkali hydrides led to different results depending on the Zr/MH ratio, the solvent, and the nature of the alkali metal (5). In the case of **4**, for example, the reaction must be carried out in THF with a rigorous Zr:KH 1:1 ratio.

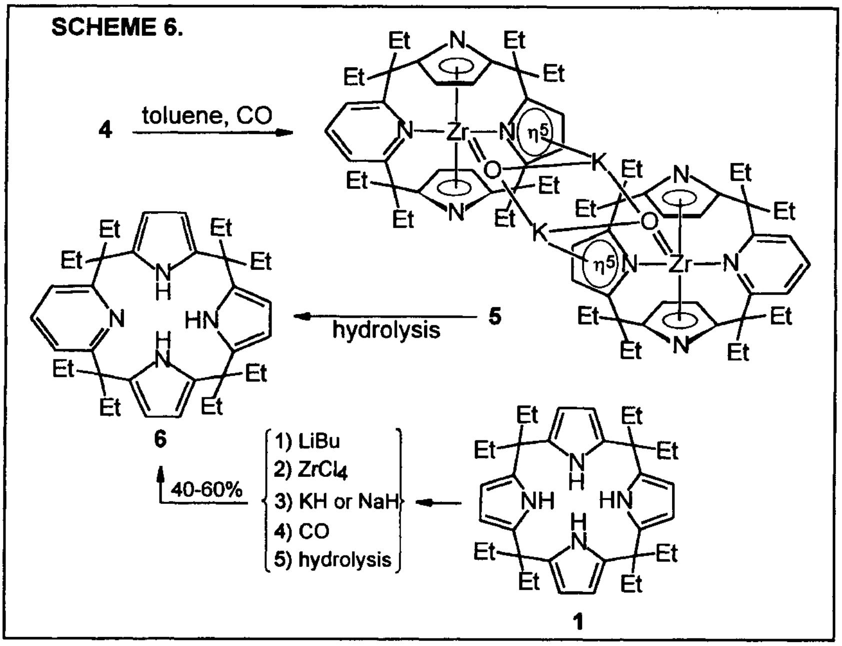
3. The homologation of the porphyrinogen using carbon monoxide

The homologation (13) of porphyrinogen involves the introduction of one carbon atom into one or two pyrrole rings, as depicted in Scheme 2. Such an homologation of pyrrole to pyridine leads to otherwise hardly accessible tris-pyrrole-monopyridine and bis-pyrrole-bis-pyridine porphyrinogen-based macrocycles (5e,7).

The homologation of pyrrole to pyridine has been successfully achieved by exploiting some well known organometallic reactions, for example the insertion of carbon monoxide into Zr-H and Zr-C bonds *via* the migration of the hydride and alkyl ligands (10,14). This often-studied reaction produces carbenium ion η^2-formyl and η^2-acyl groups (14). The carbenium ion, when sterically protected towards dimerization (which would yield an enediolato complex) or reduction, reacts as such. In the present report we describe the addition of a carbenium η^2-formyl or η^2-acyl to a pyrrole ring, followed by the complete cleavage of a C-O multiple (15) bond due to the presence of a very oxophilic metal center such as zirconium, hafnium, niobium and potassium.

The *meso*-octaethylporphyrinogen ligand exhibits some interesting characteristics which assist the transformations mentioned above. Specifically, the conformations, derived from sp^3 carbons in the *meso*-positions, and the porphyrinogen to zirconium bonding modes (5) create cavities (6,7) assuring the stabilization of reactive intermediates at the metal, and the geometrical proximity of reactive sites (pyrroles). Further, the electron rich periphery of porphyrinogen is capable of binding an alkali cation (4-9) and as will be seen, this property is of major assistance in the homologation reaction pathway.

SCHEME 6.

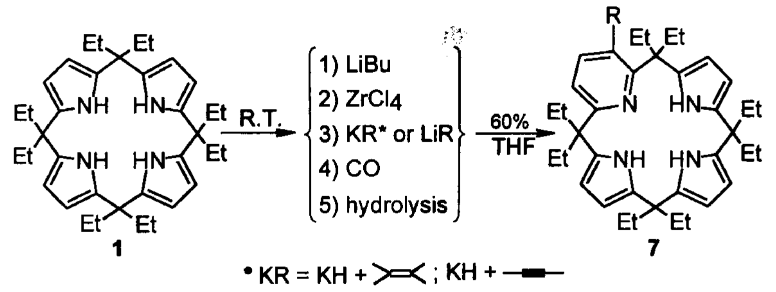


It is the reaction of these metal hydride bridged dimers with carbon monoxide which paves the way for the pyrrole to pyridine transformation. The migratory insertion reactions of carbon monoxide with Zr-H (and Zr-C) bonds have mostly focused on cyclopentadienyl and alkoxo-based systems (10,14). The analogous reaction performed with **4** emphasizes the unusual roles that porphyrinogen can play as an auxiliary ligand. Indeed, the ability to bind alkali metal cations has already been alluded to. Furthermore, the considerable three dimensional bulk of the ligand provides the necessary steric protection for the organometallic functionality.

The absorption of carbon monoxide by **4** is a rather slow reaction requiring two days, but it nonetheless produces a white crystalline solid, **5**, in high yield (78%) (Scheme 6).

The hydrolysis of **5** with H_2O under mild conditions gave 90% of the free *meso*-octaethylmonopyridinetrispyrrole macrocycle **6**. We have investigated the synthesis of **6** as either a multiple step or a one pot synthesis, and on a large scale. Both strategies gave comparable yields of 40-60% and we are now able to produce **6** in quantities of up to 50 g. The entire sequence leading to **6** from $Et_8N_4H_4$ is summarized in Scheme 7 and works equally well when NaH is used.

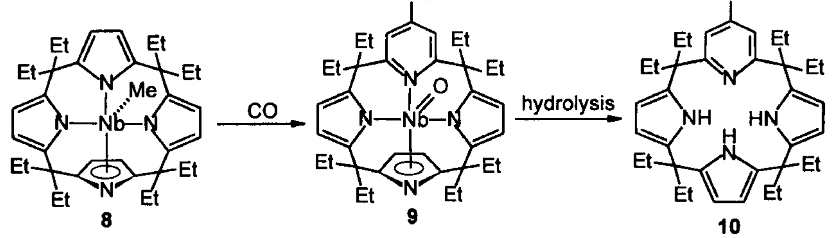
SCHEME 7.



Let us consider the genesis of **5**. The insertion of carbon monoxide into the Zr-H bond is a classic reaction in organometallic chemistry (10,14). The reaction proceeds initially to the formation of a η^2-formyl species driven by the strong oxophilicity of the metal, and then, in the absence of any steric protection, to a number of possible outcomes (14). Thus we can envisage in our case the electrophilic attack of the carbenium η^2-formyl (16) on the pyrrole followed by ring expansion (17). The preliminary step of this reaction is reminiscent of the acylation of pyridine (18) which occurs *via* the intermediate formation of η^2-acyl functionalities.

The reactions involved in Scheme 7 emphasize the role of the oxophilic zirconium and potassium ions in enhancing the carbenium ion nature of the formyl functionality (16) (*vide infra*). The stoichiometric result of the reaction is the homologation of the pyrrole to pyridine (17) by a 'CH' unit as a consequence of a complete cleavage of the C-O bond. The oxygen from the CO molecule then forms a rare example of a terminal zirconyl unit (19).

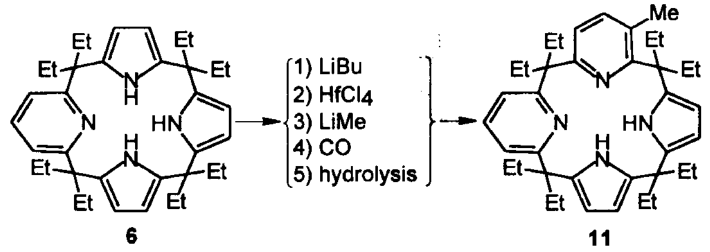
SCHEME 8.



A major stereochemical consideration should be addressed in the pyrrole to pyridine conversion that is, the regiochemistry of the homologation reaction. As the result of attack by a carbenium ion on the pyrrole ring, the formyl carbon should be in the *meta*-position of the final pyridine fragment. Such a regiochemistry is that observed in the ring expansion pyrrole→pyridine when using carbenes (17). In order to confirm such a regiochemistry we studied the reaction of Zr-alkyl derivatives **5** with carbon monoxide. This led to *meta*-substituted pyridines exclusively (Scheme 7).

Attempts to modify the regiochemistry of the homologation of the *meso*-octaethylporphyrinogen, $[Et_8N_4H_4]$, and to proceed further with the homologation of a second pyrrole ring have been successfully negotiated using metals other than zirconium. For instance, the use of niobium allowed a modification of the regiochemistry of the substitution at the pyridine ring in the homologation of $[Et_8N_4H_4]$ to the corresponding trispyrrolemonopyridine macrocycle. This has been performed according to Scheme 8 (7b).

SCHEME 9.



The regiochemistry determined by niobium is different from that imposed by zirconium, and may be due to different orientation and bonding mode of the pyrrole to the metal. An η^3-bonding mode of the pyrrolyl anion to niobium may be responsible for orientating the pyrrole β-carbon into a position susceptible to electrophilic attack and thus for the formation of a *p*-methylpyridine instead of a *m*-methyl pyridine. This explanation emphasizes the ability of the pyrrolyl anion in the porphyrinogen complexes to display different bonding modes and to fluctuate within a complex (5).

For the second homologation, we proceeded as shown in Scheme 9. The compulsory use of Hf instead of Zr is still obscure. The organometallic pathway leading from **6** to **11** is quite similar to that clarified for the homologation of **1** to **6** (Scheme 6).

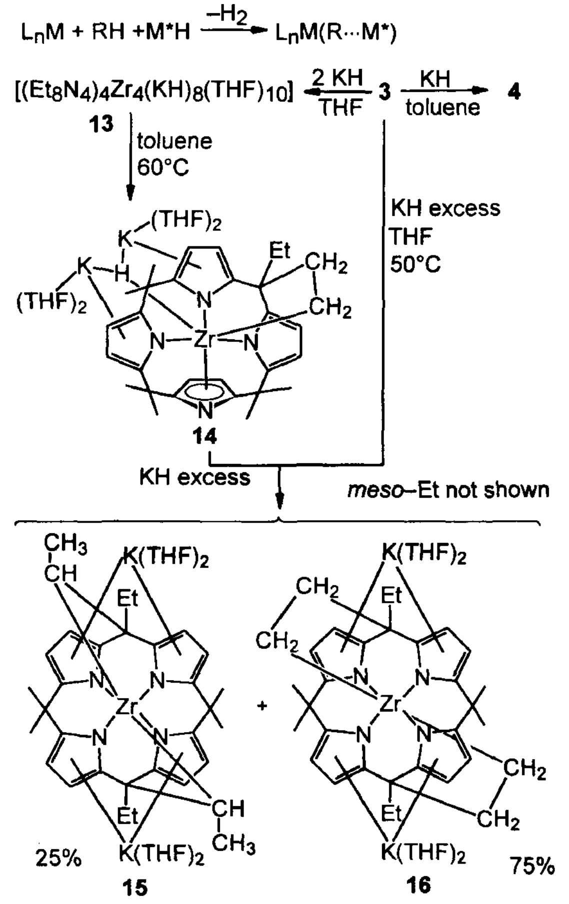
Among the two positional isomers (consider the two non-equivalent *meta* positions), that shown in Scheme 9 is the only one we have identified. The selective formation of only one regioisomer having two *cis* pyridine rings (see compound **III** in Scheme 2) aids our understanding of the homologation mechanism. Based on the structure of [$Et_8(C_4H_2N)_3(C_5H_3N)Hf\text{-}Me$], **12**, in the solid state, supported by the solution structure (^{1}H NMR spectroscopy), the homologation occurs only on the η^5-bonded pyrrole and leads exclusively to the *cis* isomer **III** (Scheme 2). It seems very likely that the η^5-pyrrolyl anions have the appropriate spacial orientation and proximity for a facile attack by the carbenium ion formed from the carbon monoxide insertion. The regiochemistry of both homologation reactions depends on the bonding mode of the ligand, which is directly determined by the nature of the transition metal.

The results reported emphasize how we can modify the skeleton and control the related regiochemistry of rather complex structures, like those of macrocyclic polypyrroles, using organometallic methodologies. In addition, this does not remain just a chemical curiosity, since we can use this transformation as a good preparative method for a novel class of macrocycles. The introduction of one or two pyridines into a tetrapyrrolic macrocycle greatly modifies the geometric and electronic properties of this very important class of compounds.

4. The functionalization of aliphatic chains at the porphyrinogen periphery.

Although electrophilic metal-mediated aliphatic C-H cleavage is precedented in the literature (20), its application to the functionalization of complex substrates is almost unknown. The present report deals with a novel electrophilic C-H bond activation and its application to the functionalization of the porphyrinogen skeleton.

SCHEME 10.



Unlike the usual approach, in which a metal bonded alkyl or hydride is employed to remove an aliphatic hydrogen in intra- or inter-molecular processes (20), we explored the following strategy.

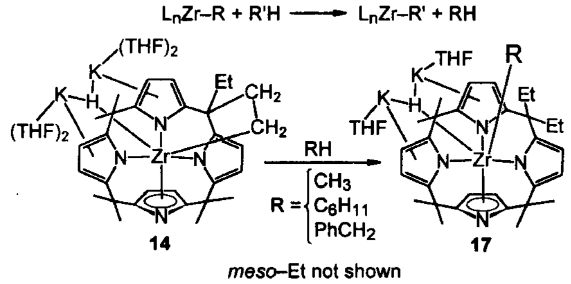
The removal of an aliphatic hydrogen by an alkali hydride M*H assisted by an electrophilic metal leads to the formation of a polar alkali metal···alkyl species complexed by L_nM (Scheme 10).

The reaction occurs when specific demands are satisfied by the ligand environment of M, particularly that allowing the L_nM complex to behave in a bifunctional manner. This allows for the complexation of alkali hydrides by the concerted action of the electron-rich periphery and the electron-deficient metal, as well as the complexation of the polar alkyl formed from the reaction (5). *Meso*-octaethylporphyrinogen, **1**, provides the appropriate ligand environment to metals for the formation of such bifunctional complexes (5-8). In addition the calix[n]arene-type conformations of the porphyrinogen (21) allows the *meso*-ethyl substituents to approach the metal, so as to assist the intramolecular deprotonation of an alkyl chain. Therefore the process depicted at top of Scheme 10 is achieved intramolecularly by the use of alkali hydrides. Such a reaction is particularly intriguing and very dependent on factors such as: *i*) the MH:Zr ratio; *ii*) the nature of the solvent; *iii*) the nature of the alkali cation. The reaction of **3** with KH exemplifies the complexity of this chemistry (Scheme 10). The reaction of **3** with one mole of KH gave the dimeric hydride **4**. When the 1:2 Zr:KH molar ratio is used we isolated the octahydride **13**, whose solid state structure has been recently elucidated (5d). In both compounds the hydrido ligands display a bridging bonding mode across Zr and K. A spontaneous thermal decomposition of **13** gave a mixture of **14**, **15** and **16**. The complete transformation of **13** into a mixture of **15** and **16** occurs only in the presence of an excess of KH. The same result is achieved when **3** is treated with a large excess of KH. Compound **14** has never been obtained pure using this strategy, but rather by alkali cation exchange reaction on **18** (*vide infra*). The **15**:**16** ratio is constant both in solution and in the solid state regardless of the genesis.

Some significant insights into the metalation of the ethyl substituents come from the careful examination of the reaction between **3** and KH under various conditions. The zirconocene hydrido functionality has been around for a long time in organometallic chemistry, and it has been involved in a number of key reactions such as hydrozirconation (12) and the reduction of carbon monoxide (14). The bonding mode of the hydride to Zr is usually either terminal or bridging. However, an alternative heterodimetallic bridging mode has been observed in complexes **4**, **13** and **14** and for some other very electrophilic metals such as Y and Al (22). This heterodimetallic interaction may be the key factor determining both the strength and the polarization of the metal-hydrogen bond appropriate for the metalation of C-H functionalities.

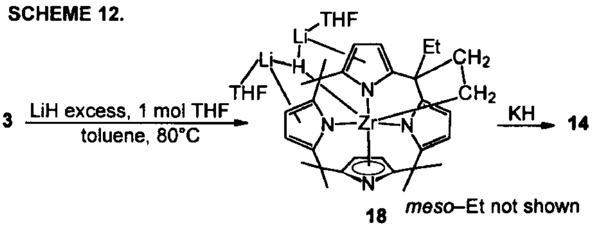
The isolation of the mixture of **15**+**16** did not clarify the genesis of the side chain metalation and the relationship between **14** and **15**+**16**. To this purpose we performed a number of experiments. We found that the isomeric **15** vs **16** ratio remains the same when **14** is heated in the presence of excess KH using similar conditions to those of the reaction performed on **3** and **13**. The result outlined above can be accounted for if the zirconium-carbon bond exchanges easily in an intramolecular fashion with the C-H bonds of other side chains of the porphyrinogen ligand. This can account for the transformation of **14** metalated exclusively at the β-carbon of the ethyl group, to give the mixture of **15** and **16**, metalated at the α and β carbons of the ethyl group, respectively. This form of σ-bond metathesis of Zr-C and C-H bonds has much precedent in high valent early transition and lanthanide metals (20).

SCHEME 11.



Further confirmation has been found in the intermolecular activation of hydrocarbon with the metalated form like **14** (Scheme 11). The alkali ion plays a major role in the metalation reaction. Using LiH and NaH, even under very drastic conditions and in a large excess, the reaction ends to the monometalated form **18** (Scheme 12). The alkali cation is very labile and can be exchanged to form the potassium derivative **14**. A particular property associated with the potassium derivative is its ability to undergo intermolecular σ-metathesis, as shown in Scheme 11.

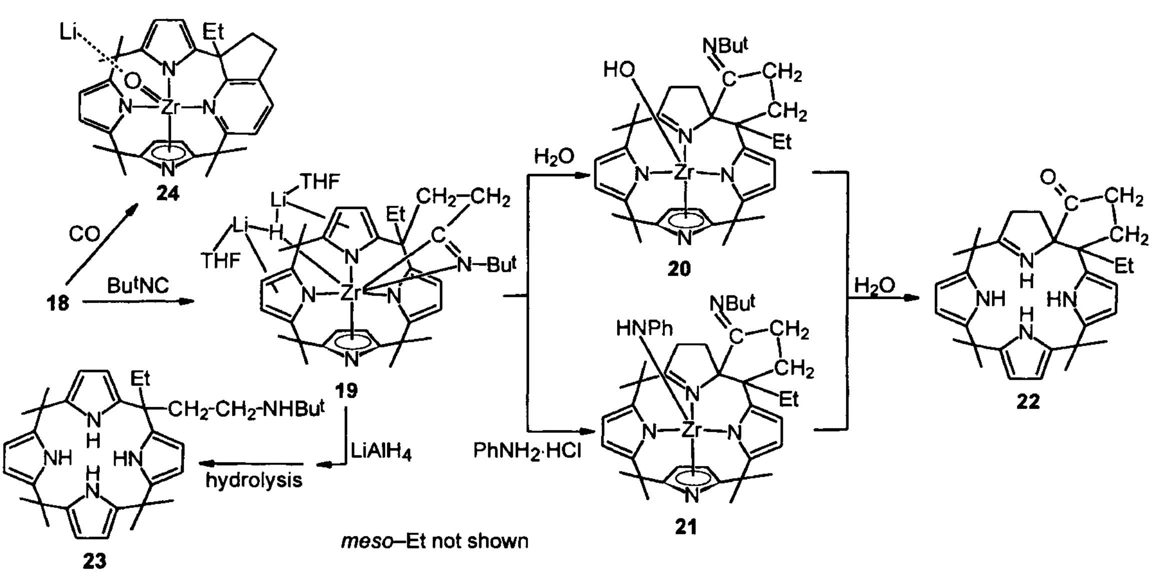
SCHEME 12.



The Zr-C bonds made *via* the intramolecular metalation of the porphyrinogen periphery should allow its easy functionalization using conventional organometallic methodologies. Among the reactions that have been explored, we report the insertion of isocyanides and carbon monoxide. Some of the more significant results are summarized in Scheme 13.

In conclusion we can say that the metalation of aliphatic chains at the periphery of *meso*-octaethylporphyrinogen has been achieved *via* the electrophilic activation of the C-H bond followed by the removal of the β-proton using alkali hydrides. The success of such a class of reactions depends on two important features. Firstly, the bifunctional nature of metal-porphyrinogen complexes which possess the ability to bind cations at the electron rich periphery, and thus to function as polar organometallic carriers. Secondly, reactivity is very dependent on the conformation of the porphyrinogen which allows the C-H bond of the periphery to come in close proximity to the central electrophilic metal. An intramolecular σ bond metathesis between Zr-C and C-H bonds was observed in the conversion of β- to α-metalated forms of the ethyl groups of porphyrinogen. The migratory insertion of Bu^tNC and carbon monoxide into the Zr-C bond allowed the introduction of functionalities at the periphery of the porphyrinogen and the attainment of novel forms of porphyrinogen. In particular, the insertion of Bu^tNC into the Zr-C bond of the monometalated form **18** allowed us to isolate the corresponding η^2-iminoacyl **19**. Its carbenium ion properties were exemplified when it underwent hydrolysis reactions (Scheme 13). The electrophilic carbenium ion attacks the α-carbon of a pyrrole to give a functionalized five-membered ring in **22**. Complexes **20** and **21** can be considered as a model intermediates in the homologation of pyrrole to

SCHEME 13.



pyridine in the reaction with carbon monoxide. Further, the reaction of **18** with CO led directly to the homologation of one of the pyrrole rings, thus in **24** a pyrrole ring has been converted to a pyridine with a fused cyclopentene ring. The results we have reported emphasize how appropriate organometallic methodologies (bifunctional complexes, conformational effects, polar organometallic carriers) allow the activation and functionalization of aliphatic substituents in large organic molecules.

References

1. B. H. Lipshutz and S. Sengupta In *Organic Reactions*, L. A. Paquette, Ed.; Vol. 41, Chapter 2, Wiley, New York (1992). B. H. Lipshutz In *Organometallics in Synthesis, a Manual*, M. Schlosser, Ed.; Chapter 4, Wiley, New York (1994).

2. M. T. Reetz In *Organotitanium Reagents in Organic Synthesis*, Springer, Berlin, Germany (1986). M. T. Reetz, R. Steinbach, J. Westermann, R. Peter and B. Wenderoth, *Chem. Ber.* **118**, 1441 (1985). M. T. Reetz and B. Wenderoth, *Tetrahedron Lett.* **23**, 5259 (1982). R. J. Morris and G. S. Girolami, *Organometallics* **10**, 792 (1991). R. W. Quan, G. C. Bazan, A. F. Kiely, W. P. Schaefer and J. E. Bercaw, *J. Am. Chem. Soc.* **116**, 4489 (1994).

3. H. Fischer and H. Orth, *Die Chemie des Pyrrols*, p 20, Akademische Verlagsgesellschaft, Leipzig (1934). M. Dennstedt and J. Zimmermann, *Chem. Ber.* **20**, 850 and 2449 (1887); **21**, 1478 (1888). D. Dennstedt, *Chem. Ber.* **23**, 1370 (1890). V. V. Chelintzev and B. V. Tronov, *J. Russ. Phys. Chem. Soc.* **48**, 105 and 127 (1916). Th. Sabalitschka and H. Haase, *Arch. Pharm.* **226**, 484 (1928). P. Rothemund and C. L. Gage, *J. Am. Chem. Soc.* **77**, 3340 (1955).

4. D. Jacoby, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Chem. Soc., Chem. Commun.* 220 (1991). J. Jubb, D. Jacoby, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Inorg. Chem.* **31**, 1306 (1992). E. Solari, F. Musso, C. Floriani, A. Chiesi-Villa and C. Rizzoli *J. Chem. Soc., Dalton Trans.* 2015 (1994).

5. (a) D. Jacoby, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Chem. Soc., Chem. Commun.* 790 (1991). (b) D. Jacoby, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.* **115**, 3595 (1993). (c) A. Rosa, G. Ricciardi, M. Rosi, A. Sgamellotti and C. Floriani, *J. Chem. Soc., Dalton Trans.* 3759 (1993). (d) D. Jacoby, S. Isoz, C. Floriani, K. Schenk, A. Chiesi-Villa and C. Rizzoli, *Organometallics*, in press. (e) S. De Angelis, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Organometallics,* in press.

6. U. Piarulli, C. Floriani, A. Chiesi-Villa and C. Rizzoli *J. Chem. Soc., Chem. Commun.* 895 (1994). S. De Angelis, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc*, **116**, 5691 and 5702 (1994). C. Floriani In *Transition Metals in Supramolecular Chemistry*, L. Fabbrizzi and A. Poggi, Eds., p. 191-209, Nato ASI Series, Kluwer, Dordrecht (1994).

7. (a) D. Jacoby, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.* **115**, 7025 (1993). (b) D. Jacoby, S. Isoz, C. Floriani, A. Chiesi-Villa, and C. Rizzoli *J. Am. Chem. Soc.* **117**, 2793 (1995).

(c) C. Floriani In *Stereoselective Reactions of Metal-Activated Molecules,* H. Werner and J. Sundermeyer, Eds., p. 97-106, Vieweg, Wiesbaden (1995).

8. C. M. Kretz, E. Gallo, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.* **116**, 10775 (1994). D. Jacoby, S. Isoz, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.* **117**, 2805 (1995). S. De Angelis, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Angew. Chem., Int. Ed. Engl.* **34**, 1092 (1995).

9. S. De Angelis, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Chem. Soc., Dalton Trans.* 2467 (1994).

10. D. J. Cardin, M. F. Lappert and C. L. Raston, *Chemistry of Organozirconium and Hafnium Compounds*, Wiley, New York (1986). S. L. Buchwald and R. B. Nielsen, *Chem. Rev.* **88**, 1047 (1988). E.-I. Negishi In *Comprehensive Organic Synthesis,* L. A. Paquette, Ed., Vol. 5, p. 1163, Pergamon, Oxford (1991). E.-I. Negishi and T. Takahashi, *Acc. Chem. Res.* **27**, 124 (1994) and references therein. N. E. Schore In *Comprehensive Organic Synthesis*, L. A. Paquette, Ed., Vol. 5, p 1037, Pergamon, Oxford (1991). G. Erker, C. Krüger and G. Müller, *Adv. Organomet. Chem.* **24**, 1 (1985) and references therein. R. F. Jordan, *Adv. Organomet. Chem.* **32**, 325 (1991).

11. M. Schlosser, Organoalkali Reagents In *Organometallics in Synthesis*, M. Schlosser, Ed., Chapter 1, Wiley, New York (1994). (b) As a general reference to organoalkali metal complexes: E. Weiss, *Angew. Chem., Int. Ed. Engl.* **32**, 1501 (1993).

12. J. Schwartz and J. A. Labinger, *Angew. Chem., Int. Ed. Engl.* **15**, 333 (1976). E.-I. Neghishi and T. Takahashi, *Aldrichimica Acta* **18**, 31 (1985). D. J. Cardin, M. F. Lappert and C. L. Raston, In *Comprehensive Organometallic Chemistry*, G. Wilkinson, F. G. A. Stone and E. W. Abel, Eds., Vol. 3; Chapter 23.2, p 45, Pergamon, Oxford (1981). J. Schwartz, *Pure Appl. Chem.* **52**, 733 (1980).

13. For a general review on the homologation reaction of alcohols and related species, see: G. P. Chiusoli, G. Salerno and M. Foa, In *Reactions of Coordinated Ligands*, P. S. Braterman, Ed., Vol. 1, Chapter 7, Plenum, New York (1986). G. W. Parshall and S. D. Ittel, *Homogeneous Catalysis*, 2nd ed.; Wiley, New York (1992). H. M. Colquhoun, D. J. Thompson and M. V. Twigg, *Carbonylation*, Plenum, New York (1991).

14. L. D. Durfee and I. P. Rothwell, *Chem. Rev.* **88**, 1059 (1988). P. T. Wolczanski and J. E. Bercaw, *Acc. Chem. Res.* **13**, 121 (1980). C. E. L. Headford and W. R. Roper, In *Reactions of Coordinated Ligands*, P. S. Braterman, Ed., Vol. 1, Ch. 8, Plenum, New York (1986). J. A. Labinger, *Transition Metal Hydrides*, A. Dedieu, Ed., VCH, Weinheim, Germany (1992).

15. R. L. Miller, P. T. Wolczanski and A. L. Rheingold, *J. Am. Chem. Soc.* **115**, 10422 (1993) and references therein. M. H. Chisholm, C. E. Hammond, V. J. Johnston, W. E. Streib and J. C. Huffman, *J. Am. Chem. Soc.* **114**, 7056 (1992). B. C. Bates, *Angew. Chem., Int. Ed. Engl.* **32**, 228 (1993).

16. K. Tatsumi, A. Nakamura, P. Hofmann, P. Stauffert and R. Hoffmann, *J. Am. Chem. Soc.* **107**, 4440 (1985). B. D. Martin, S. A. Matchett, J. R. Norton and O. P. Anderson, *J. Am. Chem. Soc.* **107**, 7952 (1985). D. M. Roddick and J. E. Bercaw, *Chem. Ber.* **122**, 1579 (1989). P. Hofmann, P. Stauffert, M. Frede and K. Tatsumi, *Chem. Ber.* **122**, 1559 (1989). P. Hofmann, P. Stauffert, K. Tatsumi, A. Nakamura and R. Hoffmann, *Organometallics* **4**, 404 (1985). K. Tatsumi, A. Nakamura, P. Hofmann, R. Hoffmann, K. G. Moloy and T. J. Marks, *J. Am. Chem. Soc.* **108**, 4467 (1986).

17. R. L. Jones and C. W. Rees, *J. Chem. Soc. C* 2249 and 2255 (1969) and references therein. F. W. Fowler, *Angew. Chem., Int. Ed. Engl.* **10**, 135 (1971).

18. P. E. Fanwick, L. M. Kobriger, A. K. McMullen and I. P. Rothwell, *J. Am. Chem. Soc.* **108**, 8095 (1986). J. Arnold, T. D. Tilley and A. L. Rheingold, *J. Am. Chem. Soc.* **108**, 5355 (1986).

19. W. A. Howard, M. Waters and G. Parkin, *J. Am. Chem. Soc.* **115**, 4917 (1993).

20. J. A. Davies, P. L. Watson, J. F. Liebman and A. Greenberg, *Selective Hydrocarbon Activation*, VCH, New York (1990). *Activation and Functionalization of Alkanes*, C. L. Hill, Ed., Wiley, New York (1989). A. E. Shilov, *Activation of Saturated Hydrocarbons by Transition Metal Complexes*, Reidel, Ingham, MA (1984). W. D. Jones and F. J. Feher, *Acc. Chem. Res.* **2**, 91 (1989). A. D. Ryabov, *Chem. Rev.* **90**, 403 (1990). A. Sen, *Acc. Chem. Res.* **21**, 421 (1988). R. H. Crabtree, *Chem. Rev.* **85**, 245 (1985).

21. B. von Maltzan, *Angew. Chem., Int. Ed. Engl.* **21**, 785 (1982). C. D. Gutsche, *Calixarenes,* Royal Society of Chemistry, Cambridge, U. K. (1989).

22. M. J. Evans, H. J. Meadows and P. T. Hanusa, *J. Am. Chem. Soc.* **106**, 4454 (1984). P. C. Wailes, H. Weigold and A. P. Bell, *J. Organometal. Chem.* **43**, C29 (1972).