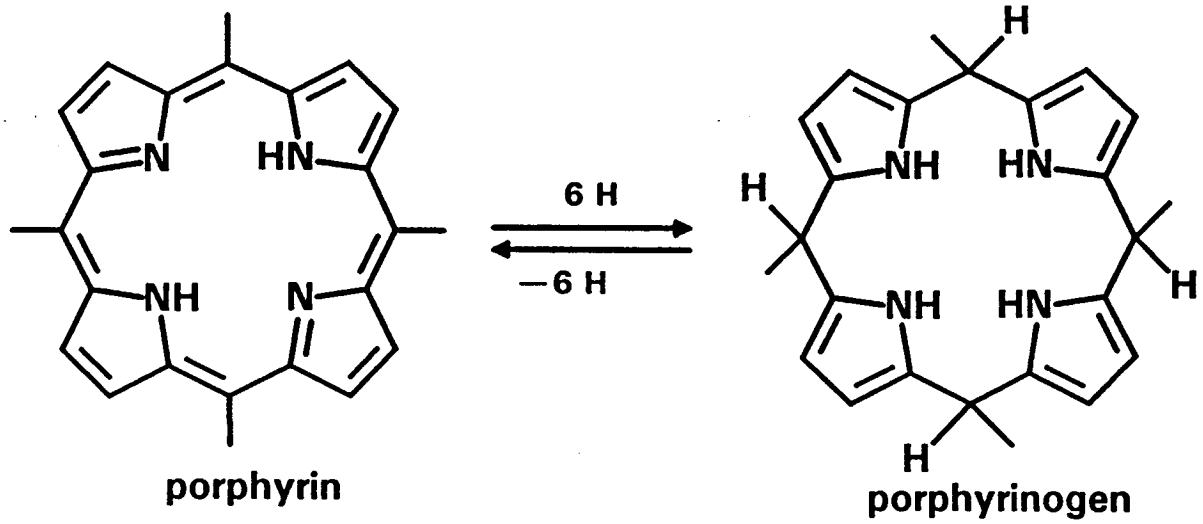
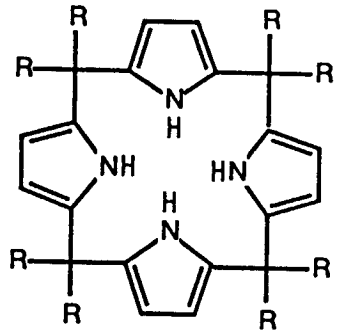
Porphyrin - Porphyrinogen relationship



porphyrin

porphyrinogen

Meso-Octaalkylporphyrinogen



a) H. Fischer and H. Orth, "Die Chemie des Pyrrols," Akademische Verlagsgesellschaft m.b.H, Leipzig, **1934**, 20;

b) A. Baeyer, *Ber.*, **1886**, 19, 2184;

c) M. Dennstedt and J. Zimmermann, *Ber.*, **1887**, 20, 850, 2449; *Ber.*, **1888**, 21, 1478;

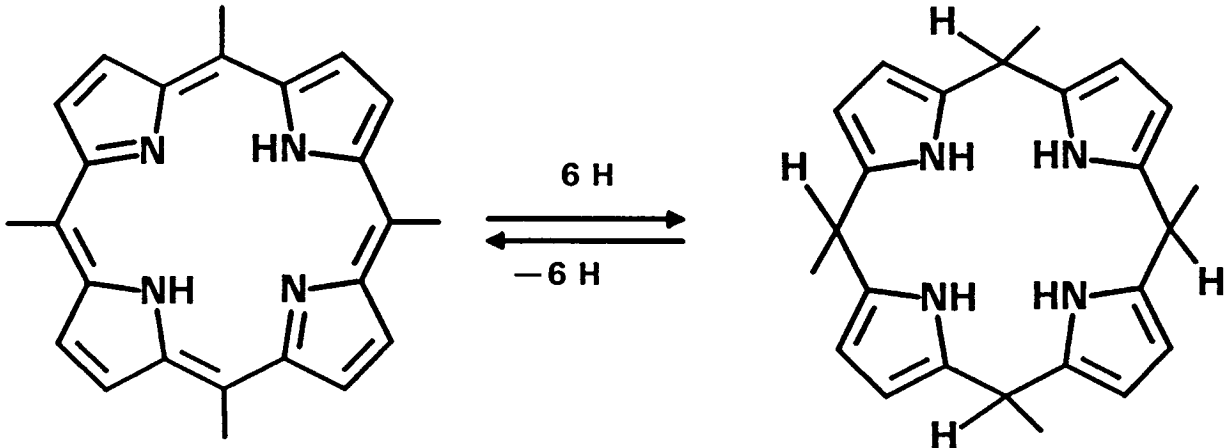
d) M. Dennstedt, *Ber.*, **1890**, 23, 1370;

e) V. V. Chelintzev and B. V. Tronov, *J. Russ. Phys. Chem. Soc.*, **1916**, *48*, 105, 127;

f) Th. Sabalitschka and H. Haase, *Arch. Pharm.*, **1928**, *226*, 484;

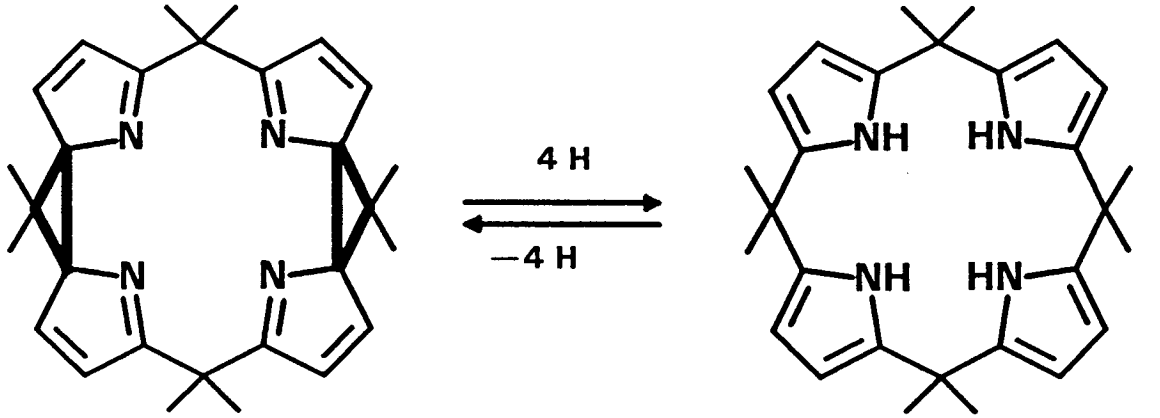
g) P. Rothemund and C. L. Gage, *J. Am. Chem. Soc.*, **1955**, *77*, 3340.

Porphyrinogen redox chemistry



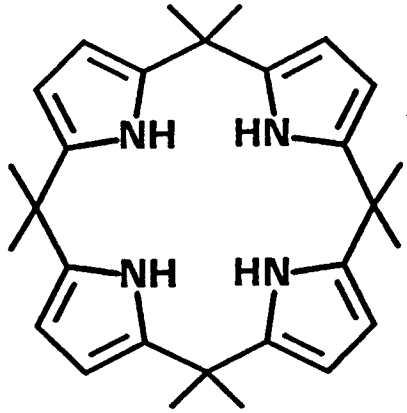
porphyrin

porphyrinogen



meso-octaalkylporphyrinogen

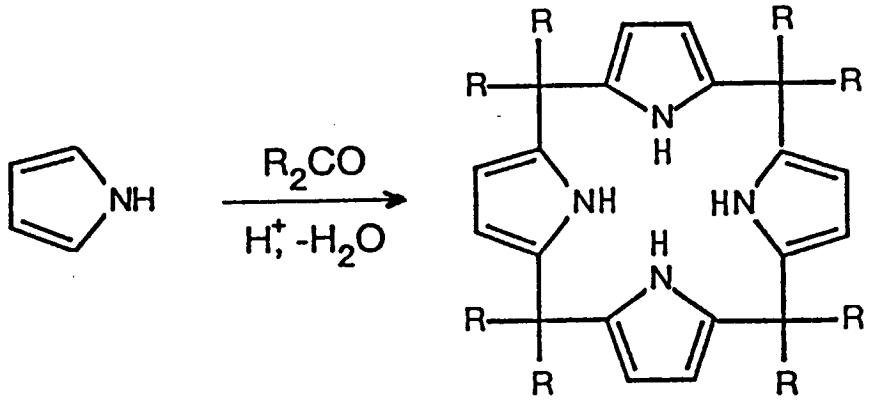
Meso-octaalkylporphyrinogen metal-assisted chemistry



Meso-octaalkylporphyrinogen, $[R_8N_4H_4]$

1) Redox chemistry based on the reversible formation of a cyclopropane unit
2) Homologation of a pyrrole to a pyridine ring assisted by the metal

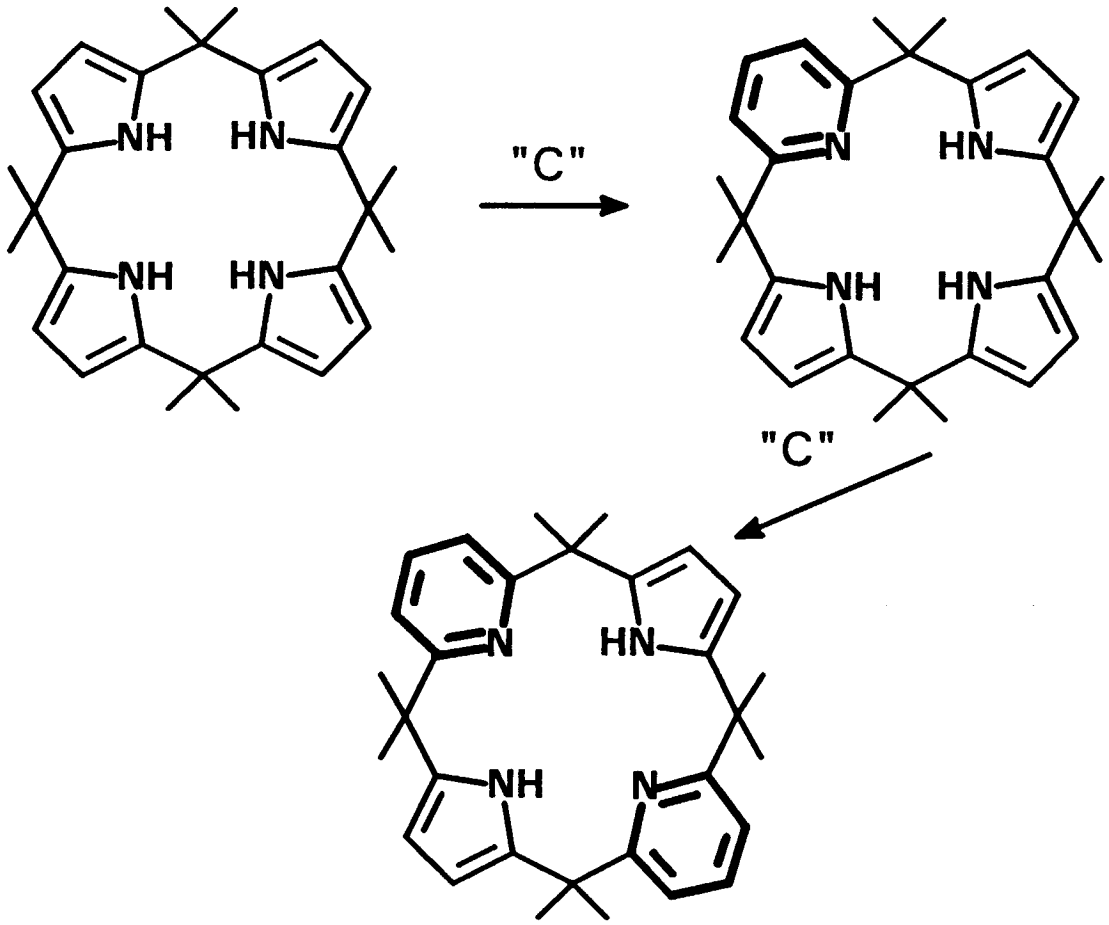
Meso-octaalkylporphyrinogen

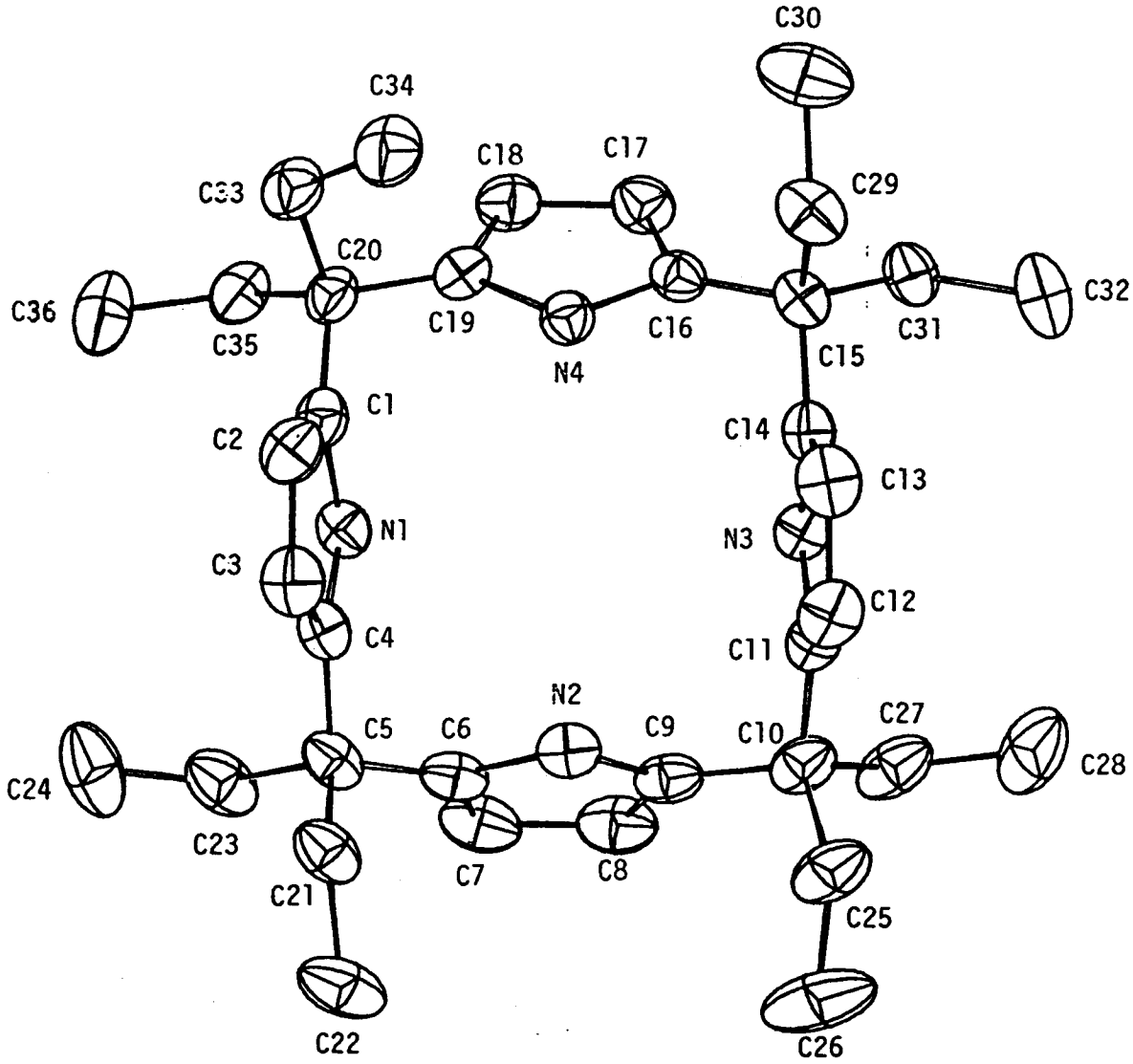


R = alkyl, cycloalkyl, functionalized alkyl, etc....

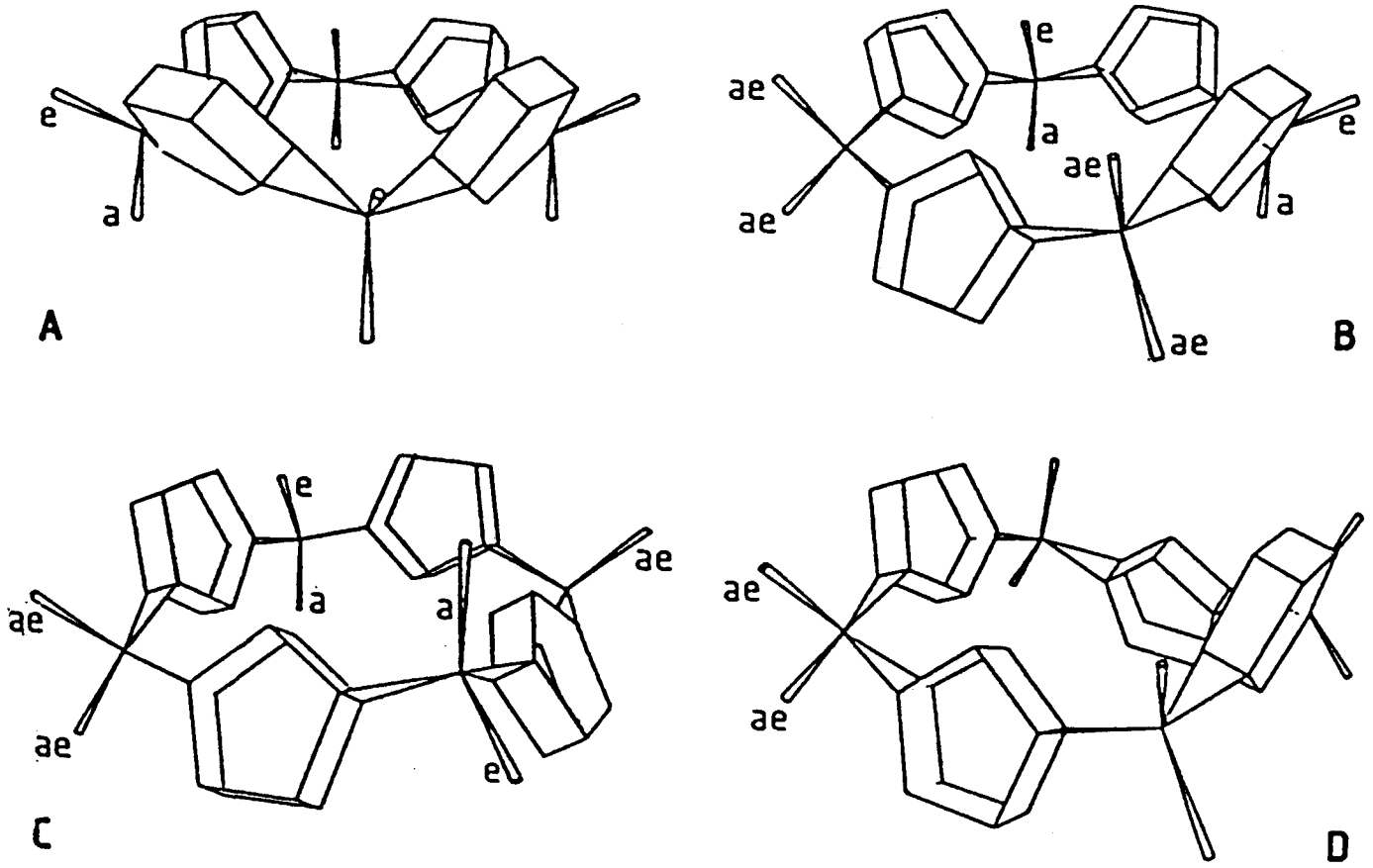
Homologation of pyrrol to pyridine ring

in *meso*-octaalkylporphyrinogens





The *saddle* conformation of $Et_8N_4H_4$



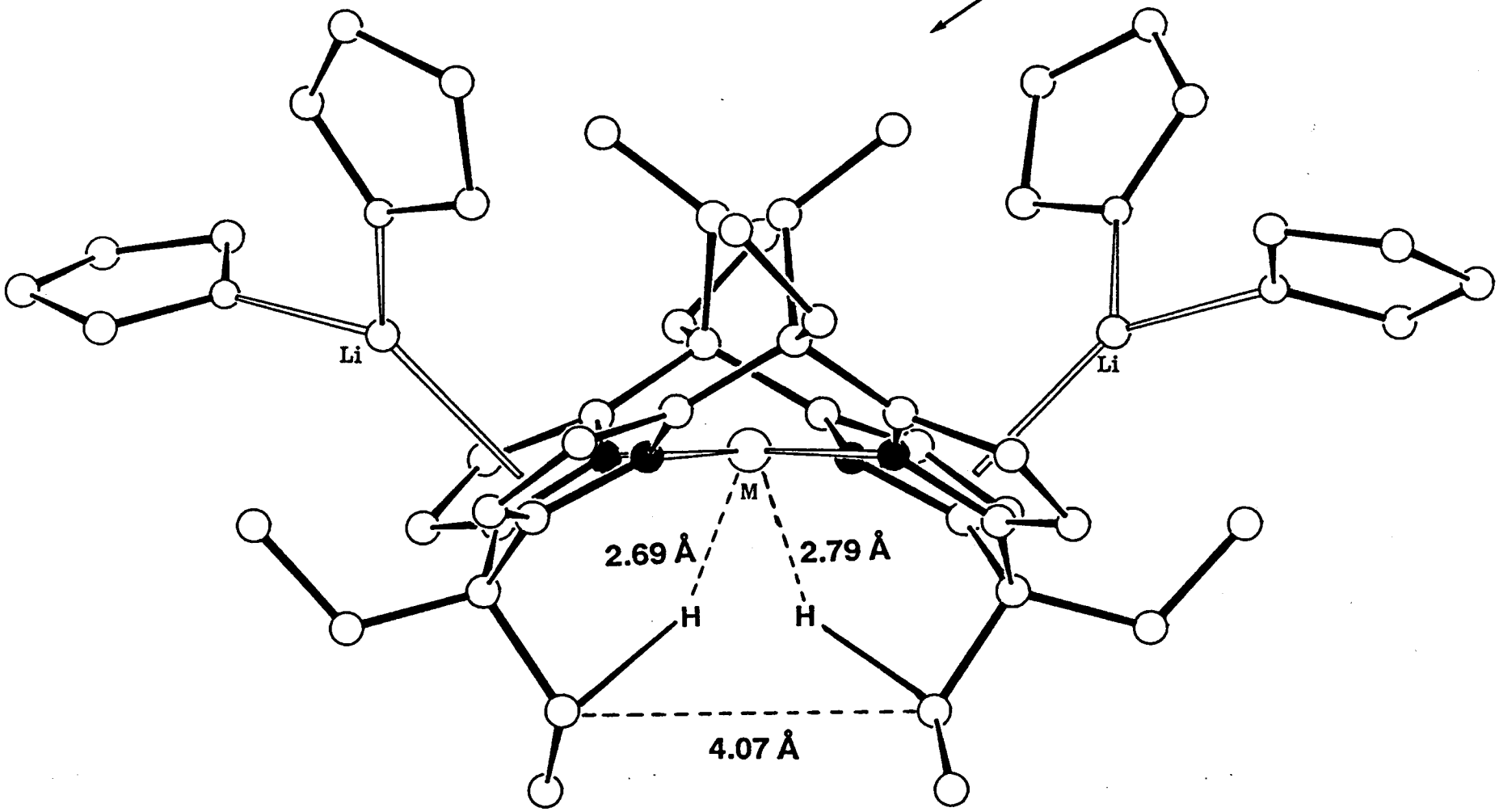
The four fundamental conformations of the porphyrinogens:

"bowl" (A), "chair" (B), "chaise longue" (C), and "saddle" (D)

(*meso*-substituents: a = axial, e = equatorial or ae = axial-equatorial)

B. von Maltzan, *Angew. Chem., Int. Ed. Engl.*, 1982, *21*, 785.

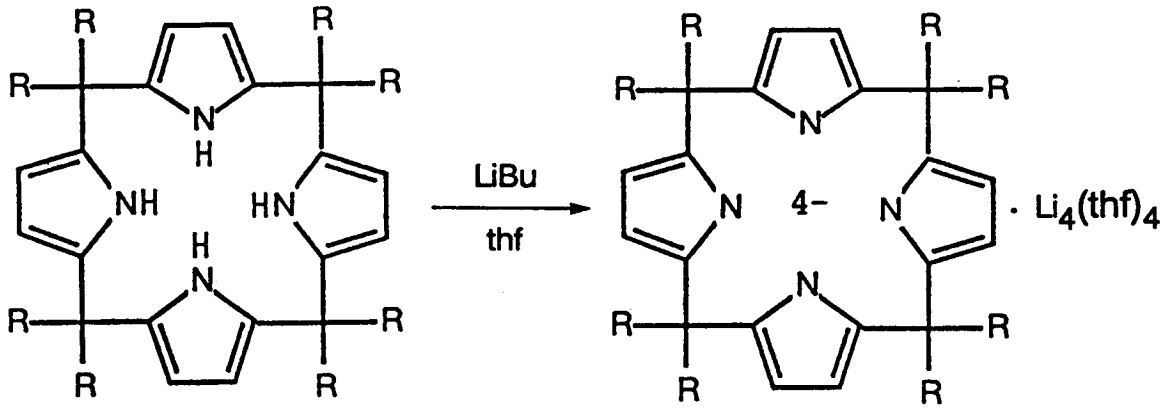
$[Et_8N_4Li_4(thf)_4] + MCl_2 \xrightarrow[-LiCl]{thf} [Et_8N_4 M Li_2(thf)_4]$



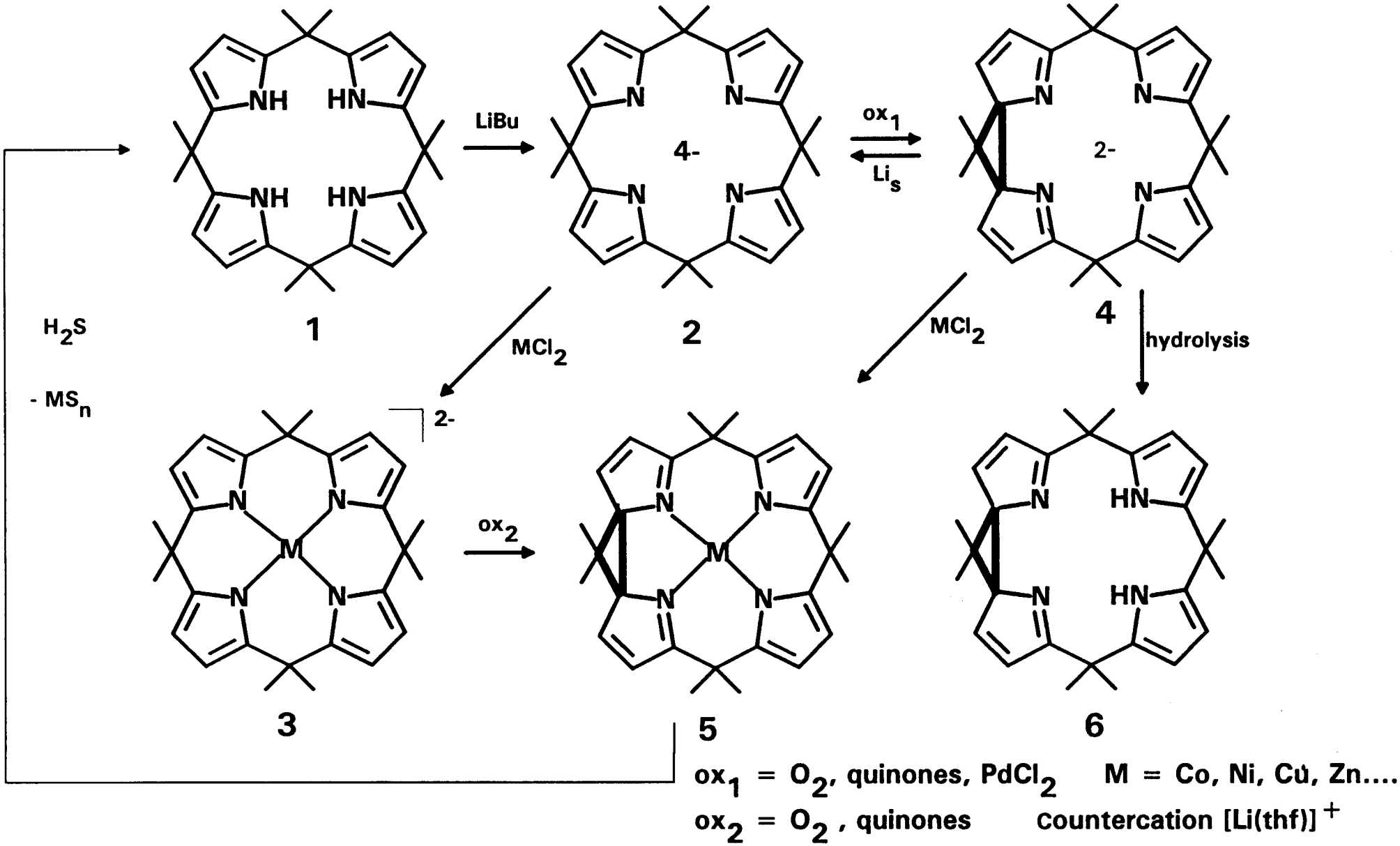
$[Et_8N_4 M Li_2(thf)_4]$

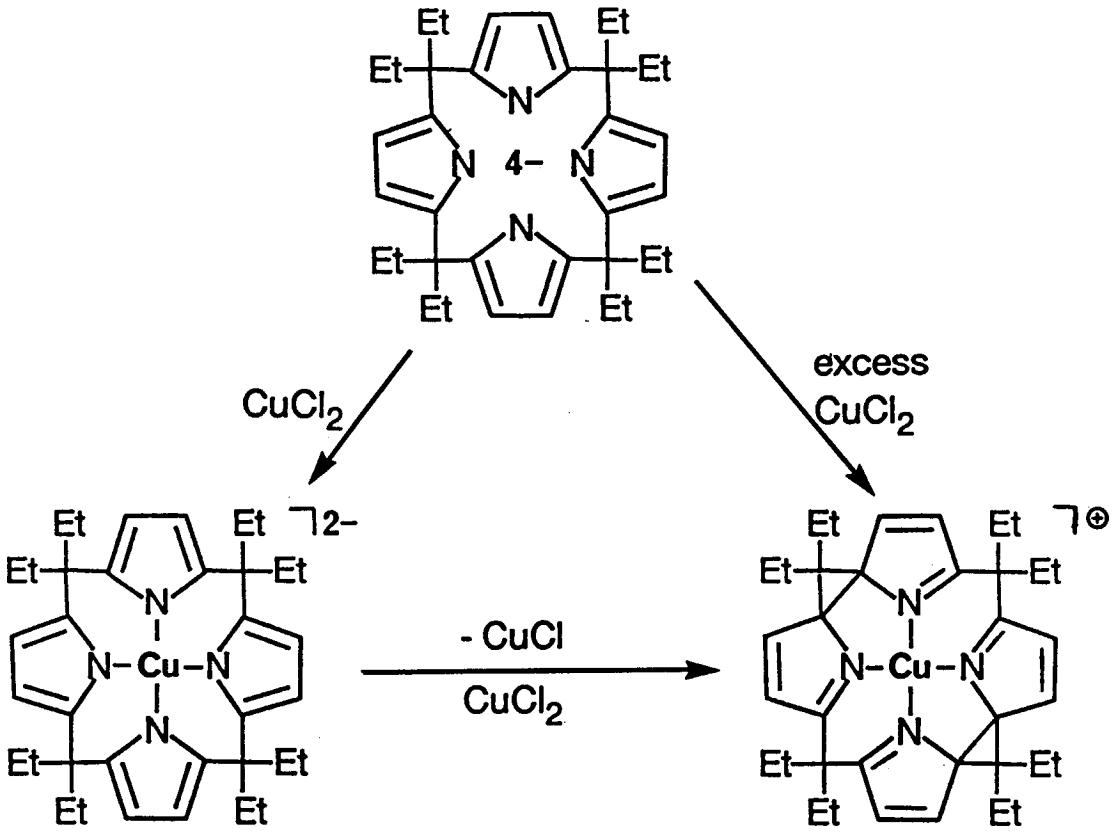
M = Fe, Co, Ni, Cu

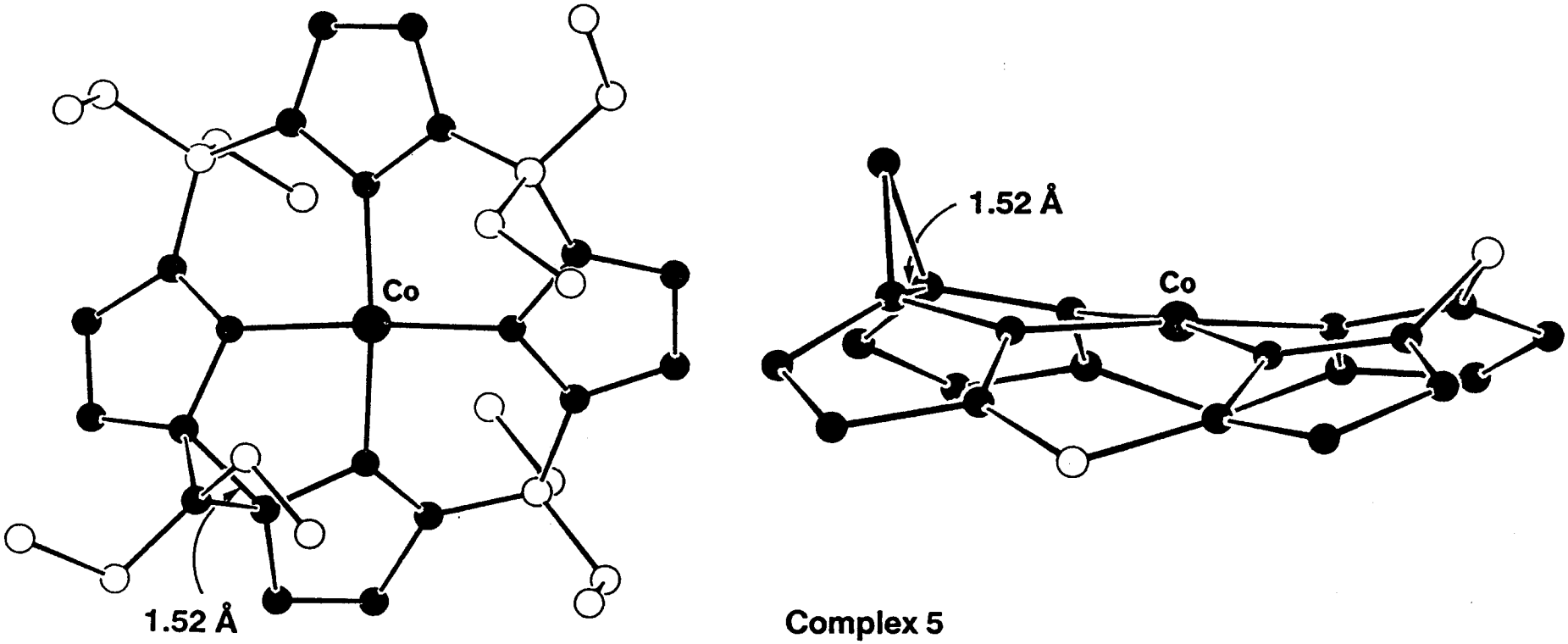
Lithium *Meso*-Octaalkylporphyrinogen



Complex 4

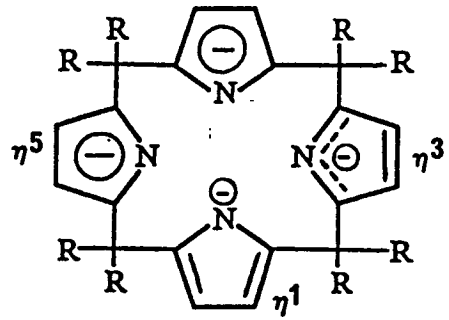

NH
HN
NH
HN
1
LiBu
N
N
4-
N
N
2
ox1
Li_s
N
N
2-
N
N
4
H2S
- MSn
MCl2
MCl2
hydrolysis
2-
N
N
M
N
N
3
ox2
N
N
M
N
N
5
N
HN
N
HN
6
ox1 = O2, quinones, PdCl2
M = Co, Ni, Cu, Zn....
ox2 = O2 , quinones
countercation [Li(thf)]+


Et
Et
Et
Et
N
N
4-
N
N
Et
Et
Et
Et
CuCl2
excess
CuCl2
2-
N
Cu
N
N
- CuCl
CuCl2
⊕



Complex 5

Meso-Octaalkylporphyrinogen Tetraanion



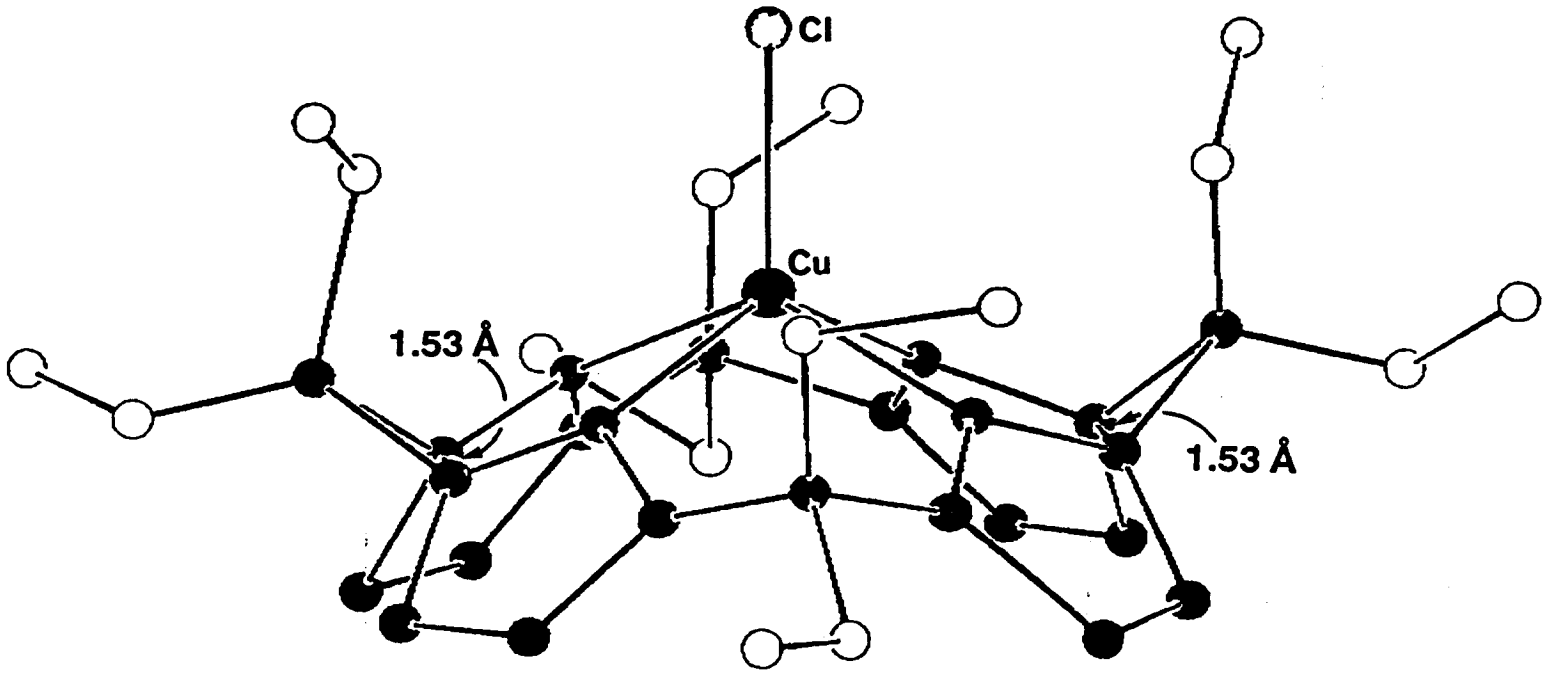
4 (2 + n) electron donor ligand

$0 < n < 4$

$8 \cdots\cdots 24$ electrons

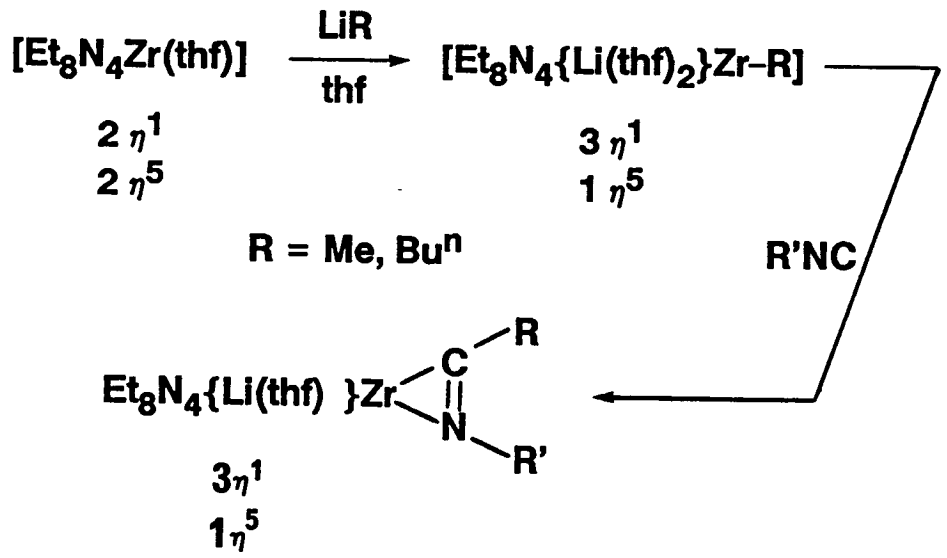
- n = 1 for η^5
- n = 1/2 for η^3
- n = 0 for η^1

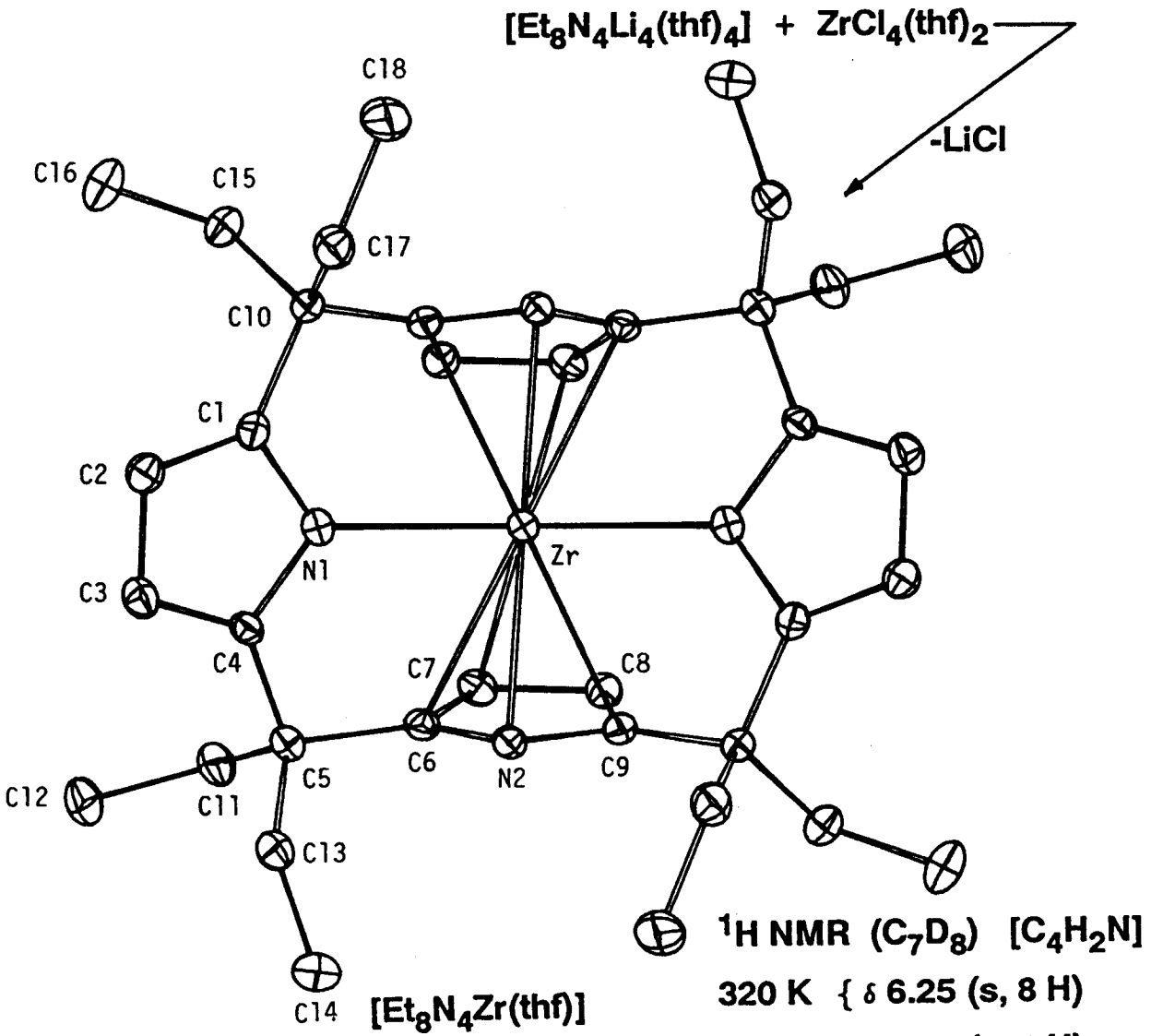
} pyrrolyl anion



$[Et_8N_4 \cdot CuCl]$

Meso-Octaethylporphyrinogen varying bonding modes



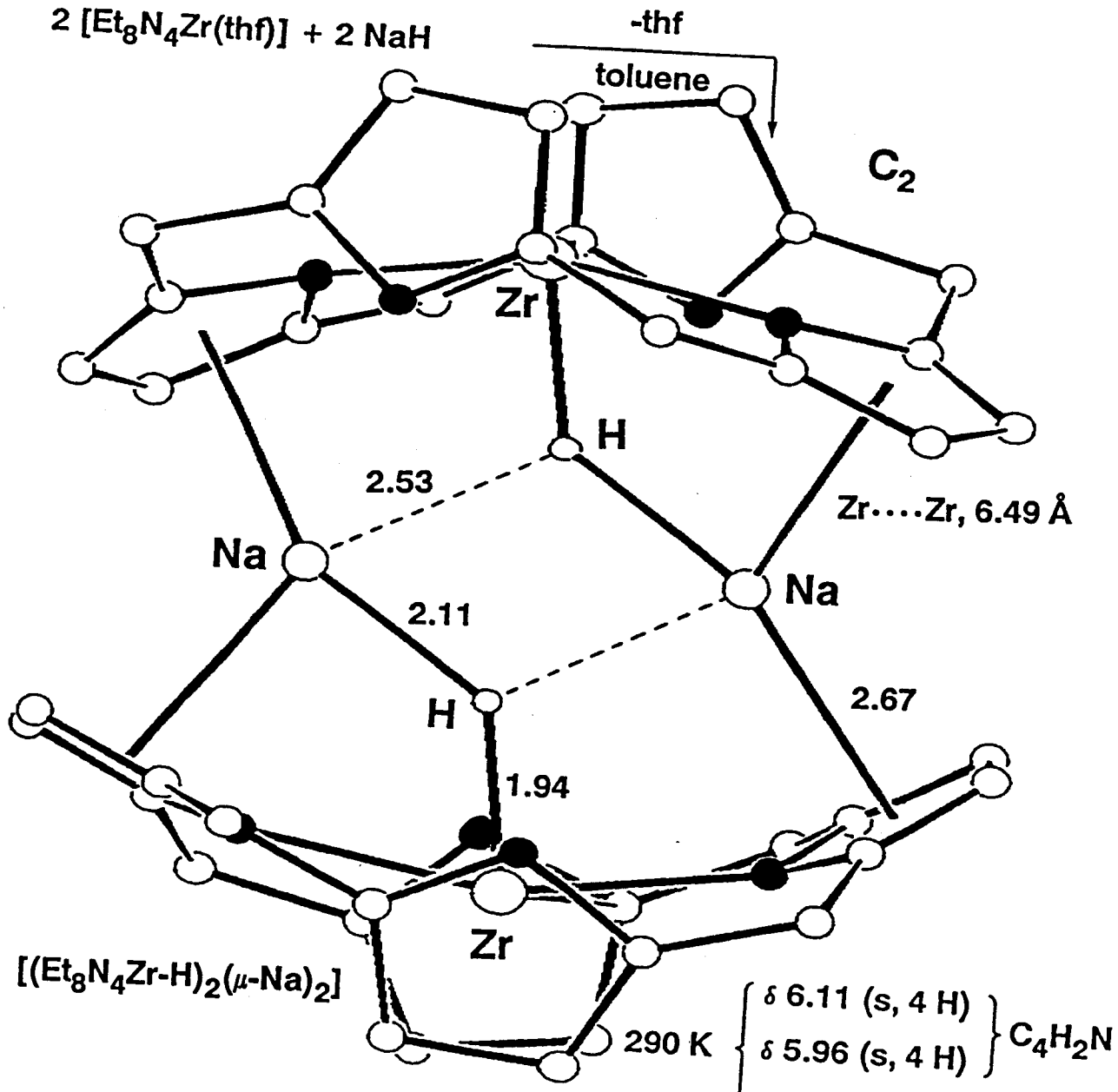


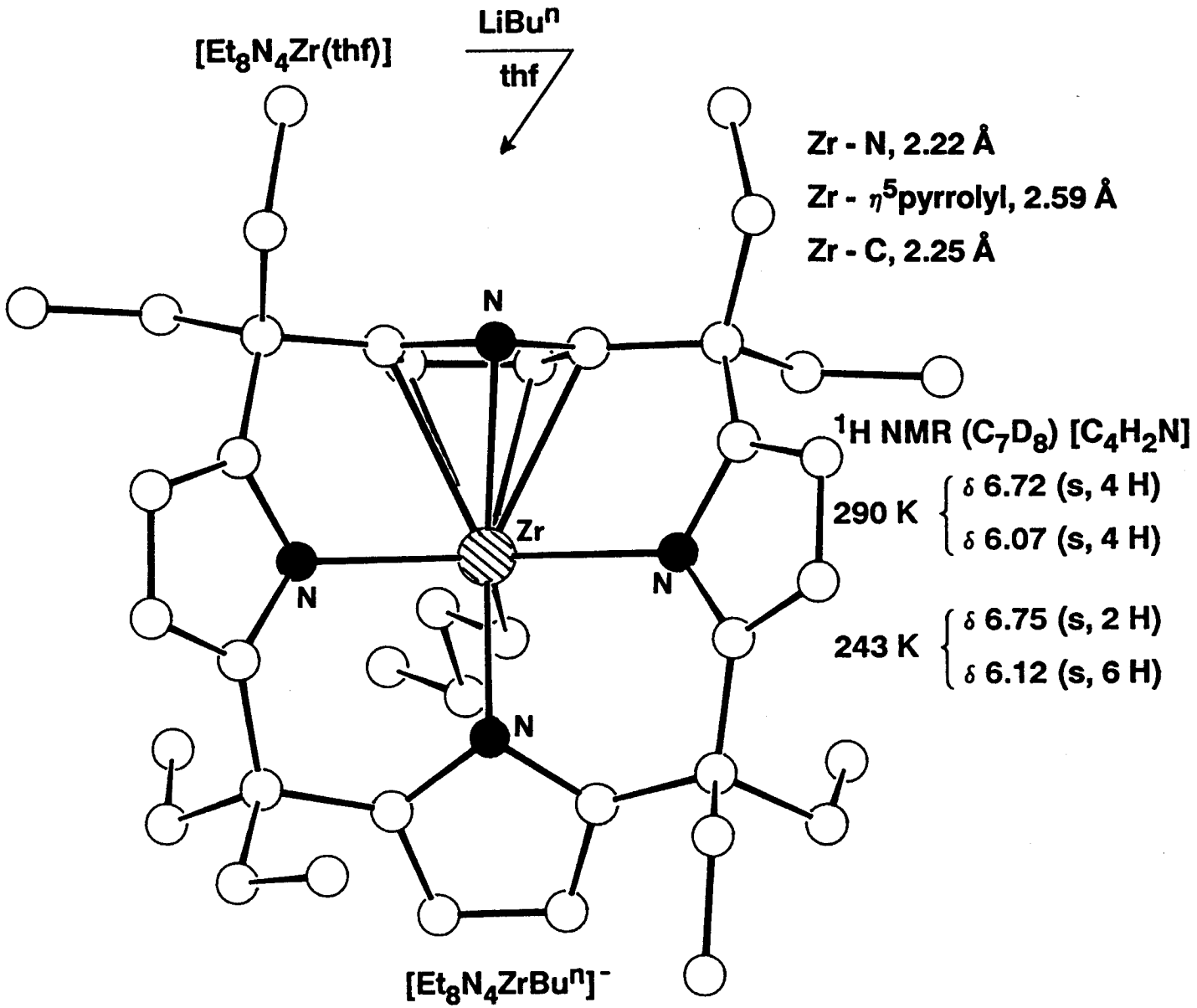
$[Et_8N_4Zr(thf)]$

^1H NMR (C_7D_8) [C_4H_2N]

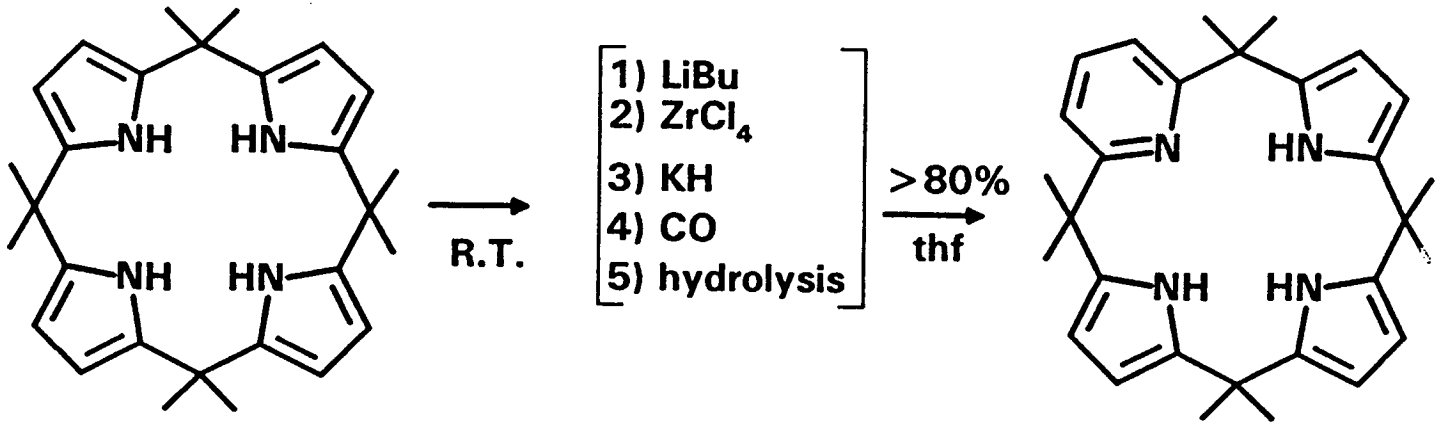
320 K { δ 6.25 (s, 8 H)

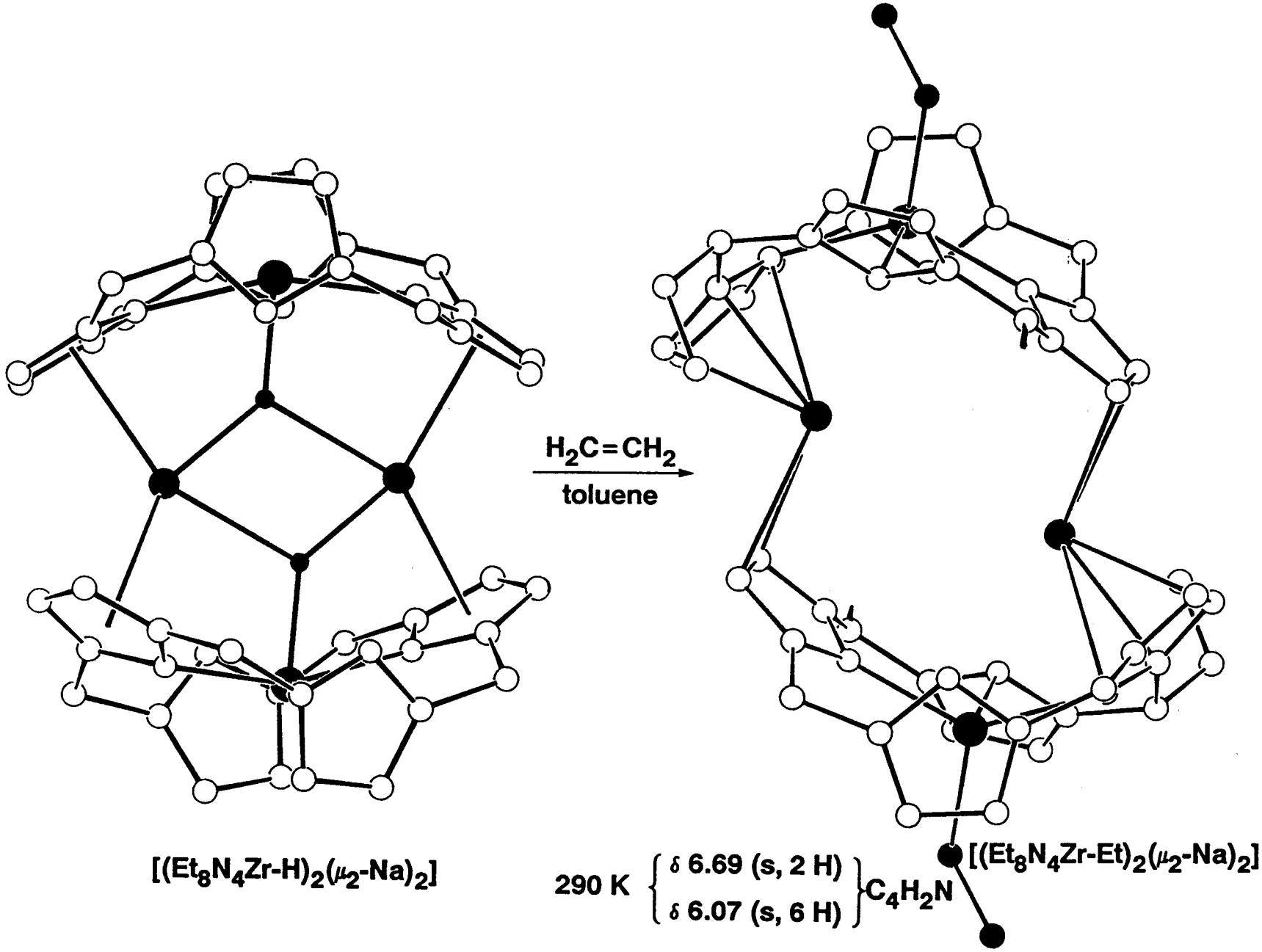
290 K { δ 6.31 (s, 4 H)
{ δ 6.24 (s, 4 H)

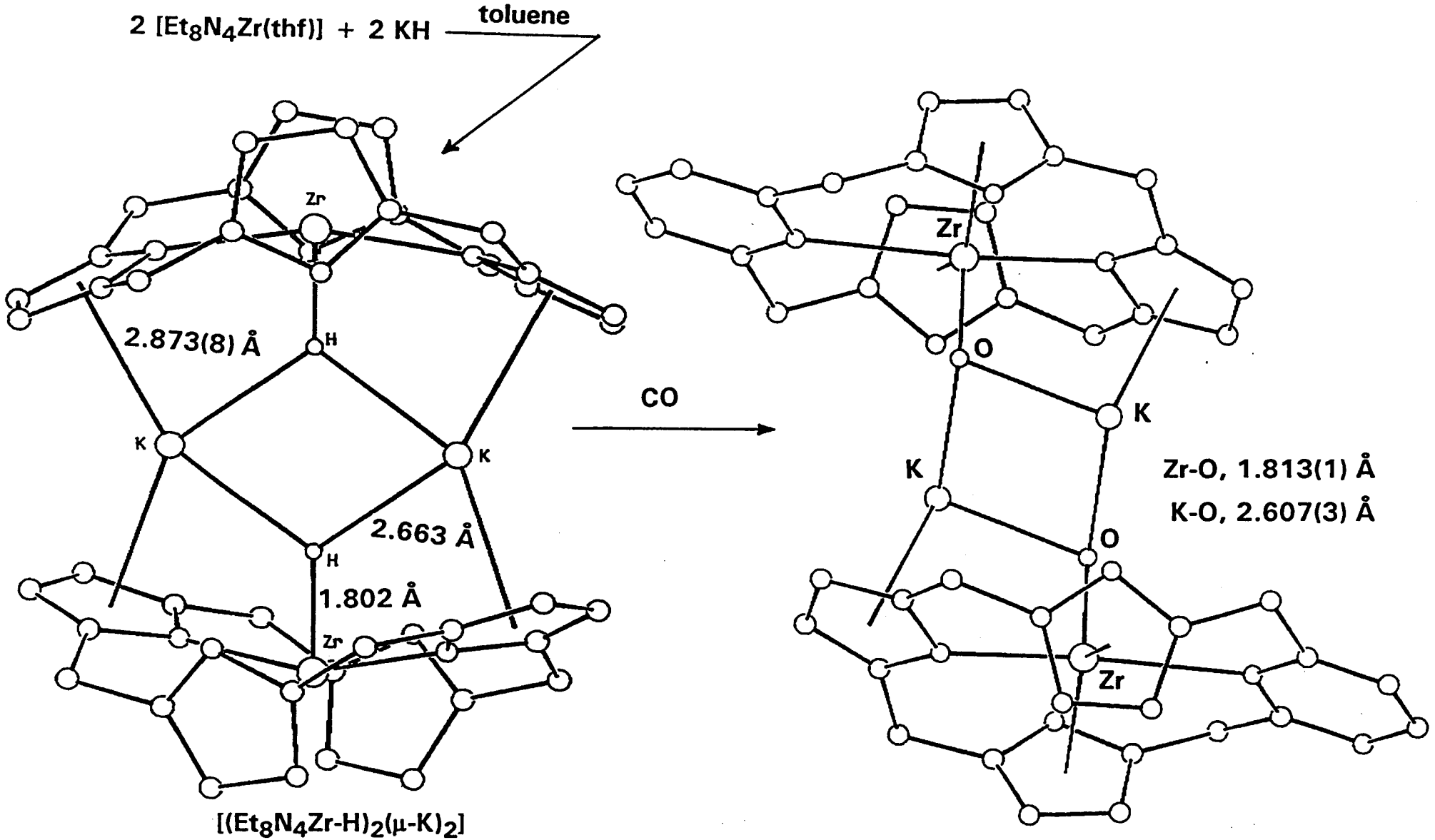

2 [Et8N4Zr(thf)] + 2 NaH
-thf
toluene
C2
Zr
H
2.53
Zr····Zr, 6.49 Å
Na
2.11
Na
H
2.67
1.94
Zr
[(Et8N4Zr-H)2(μ-Na)2]
290 K
δ 6.11 (s, 4 H)
δ 5.96 (s, 4 H)
C4H2N
δ 1.60 (s, 1 H)
Zr-H

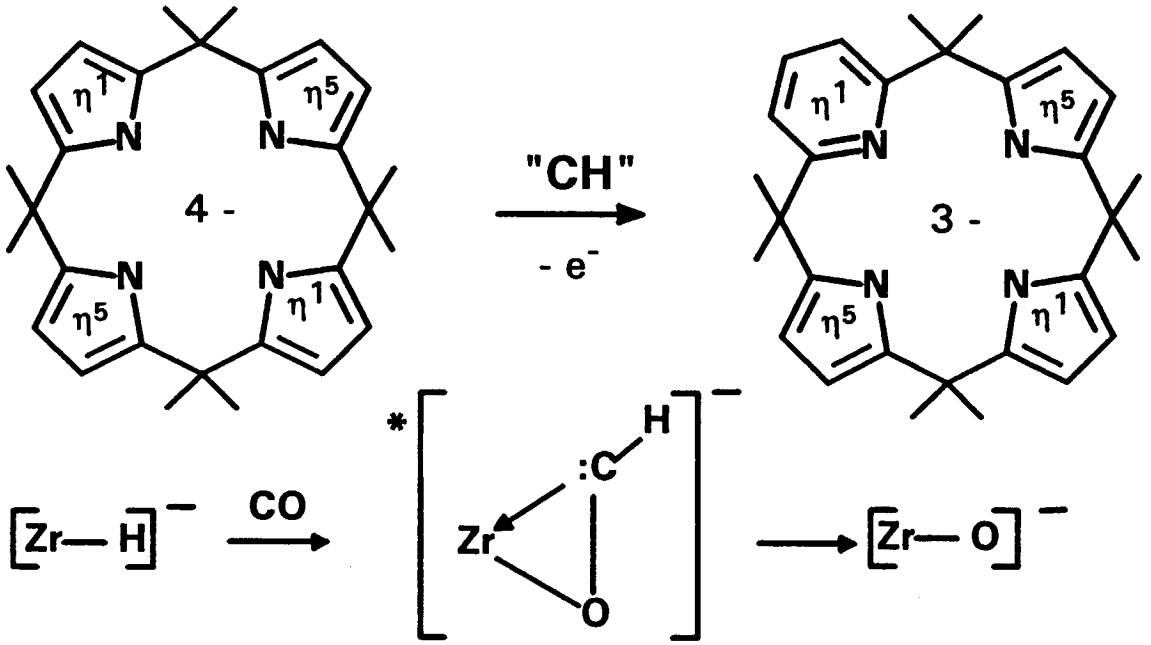

[Et8N4Zr(thf)]
LiBun
thf
Zr - N, 2.22 Å
Zr - η5pyrrolyl, 2.59 Å
Zr - C, 2.25 Å
N
Zr
N
N
N
1H NMR (C7D8) [C4H2N]
290 K
δ 6.72 (s, 4 H)
δ 6.07 (s, 4 H)
243 K
δ 6.75 (s, 2 H)
δ 6.12 (s, 6 H)
[Et8N4ZrBun]-

One step homologation reaction




H2C=CH2
toluene
[(Et8N4Zr-H)2(μ2-Na)2]
290 K
δ 6.69 (s, 2 H)
δ 6.07 (s, 6 H)
C4H2N
[(Et8N4Zr-Et)2(μ2-Na)2]


2 [Et8N4Zr(thf)] + 2 KH
toluene
Zr
2.873(8) Å
H
K
K
2.663 Å
H
1.802 Å
Zr
[(Et8N4Zr-H)2(μ-K)2]
CO
Zr
O
K
K
Zr-O, 1.813(1) Å
K-O, 2.607(3) Å
O
Zr



* see the zirconoxycarbene chemistry: I.P. Rothwell, *Chem. Rev.*, **1988**, *88*, 1059