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Zirconium-Assisted Homologation of Pyrrole to Pyridine in the Conversion of *meso*-Octaethylporphyrinogen into a *meso*-Octaethyltrispyrrolemonopyridine Macrocycle with Carbon Monoxide and the Structure of the First Zirconyl Complex

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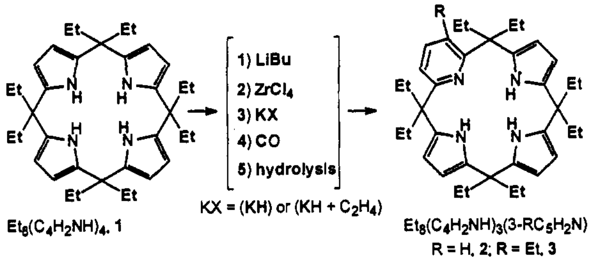
This report deals with the zirconium-mediated homologation of the tetraprotic macrocycle *meso*-octaethylporphyrinogen (**1**)[1,2] to triprotic *meso*-octaethyltrispyrrolemonopyridines **2** and **3**, using carbon monoxide as the homologating reagent. The sequence of reaction steps associated with the transformation of a pyrrole to a pyridine ring within the tetrapyrrole macrocycle of **1** to **2** and **3** is indicated in reaction 1.



$Et_8(C_4H_2NH)_4$, **1**

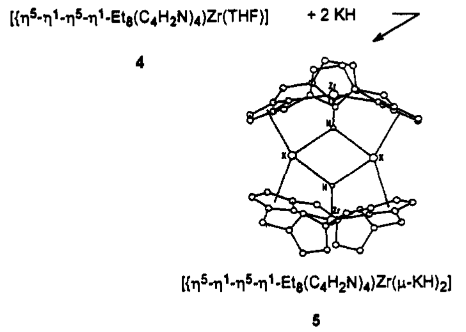
$Et_8(C_4H_2NH)_3(3\text{-}RC_5H_2N)$
R = H, **2**; R = Et, **3**

(1)

Each of the five steps of sequence 1 is high yield, and the synthesis of **2** and **3** can be carried out on a multigram scale.

The synthesis of $[\{\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_8(C_4H_2N)_4\}Zr(THF)]$ (**4**), as well as its transformation into a hydrido species, shown in the first three steps of the previous sequence, has already been reported in case of NaH.[2e]

The reaction of **4** with KH led to the dimeric hydrido complex **5**[3] (in the simplified drawing of reaction 2, the *meso*-Et groups have been omitted. The structure is similar to that of the sodium analogue[2e] and has been confirmed by X-ray crystallography.

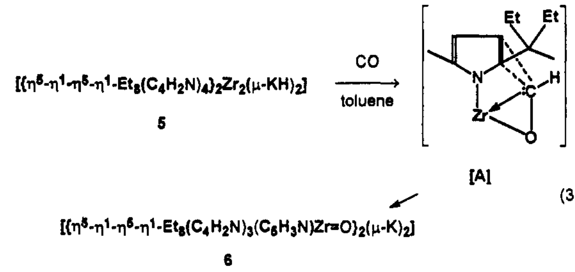


$[\{\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_8(C_4H_2N)_4\}Zr(THF)]$
4

$[\{\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_8(C_4H_2N)_4\}Zr(\mu\text{-}KH)_2]$
5

(2)

The reaction of complex **5** with carbon monoxide at room temperature (reaction 3 affords **6**[4] (80%), which has been structurally characterized.[5]



$[\{\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_8(C_4H_2N)_4\}_2Zr_2(\mu\text{-}KH)_2]$
5

[A]

$[\{\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_8(C_4H_2N)_3(C_5H_3N)Zr{=}O\}_2(\mu\text{-}K)_2]$
6

(3)

A perspective view of **6** is shown in Figure 1, while the zirconyl unit is shown in Figure 2. The trispyrrole fragment is η^5-η^1-η^5-bonded to zirconium, while the pyridine fragment interacts with the metal at a very long distance [2.669(4) Å]. The potassium cation has a strong η^5-interaction with the Zr-η^1-bonded pyrrolyl anion and with the oxo group, and it completes its coordination sphere by interacting weakly with the C30 and C34 hydrogens.[6] The Zr-O distance [1.813(2) Å] is very short[7] compared with that in the single oxo-bridged analogous zirconium compound $\{[(K)(\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_8(C_4H_2N)_4Zr](\mu_2\text{-}O)\}$ [1.975(2) Å],[7e] and it supports clearly the existence of a Zr–O double bond. The $(\eta^5\text{-}C_4H_2N)_2Zr$ fragment has a geometry approaching that of a bent $[Cp_2Zr]$ fragment.

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(1) (a) Fischer, H.; Orth, H. *Die Chemie des Pyrrols*; Akademische Verlagsgesellschaft: Leipzig, 1934; p 20. (b) Baeyer, A. *Chem. Ber.* **1886**, *19*, 2184. (c) Dennstedt, M.; Zimmermann, J. *Chem. Ber.* **1887**, *20*, 850; 2449; *Chem. Ber.* **1888**, *21*, 1478. (d) Dennstedt, D. *Chem. Ber.* **1890**, *23*, 1370. (e) Chelintzev, V. V.; Tronov, B. V. *J. Russ. Phys. Chem. Soc.* **1916**, *48*, 105; 127. (f) Sabalitschka, Th.; Haase, H. *Arch. Pharm.* **1928**, *226*, 484. (g) Rothemund, P.; Gage, C. L. *J. Am. Chem. Soc.* **1955**, *77*, 3340.

(2) Molecule **1** has been recently rediscovered as a ligand for transition metals: (a) Jacoby, D.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Chem. Commun.* **1991**, 220. (b) Jubb, J.; Jacoby, D.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1992**, *31*, 1306. (c) Jubb, J.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1992**, *114*, 6571. (d) Jacoby, D.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Chem. Commun.* **1991**, 790. (e) Jacoby, D.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1993**, *115*, 3595.

(3) Preparation of **5**: **4**[2d] (19.30 g, 27.6 mmol) and KH (1.10 g, 27.5 mmol) were refluxed in toluene (200 mL) for 48 h, and then the major part of toluene was distilled off. After cooling, a sparingly soluble yellow microcrystalline solid was obtained (88%). When this solid was recrystallized in a large amount of toluene, pale yellow crystals were obtained. Anal. Calcd for $C_{72}H_{98}K_2N_8Zr_2$: C, 64.66; H, 7.33; N, 8.38. Found: C, 65.03; H, 7.32; N, 8.18. The low solubility of this compound prevented NMR studies. Crystallographic and structural information on **5** is available in the supplementary material.

(4) Preparation of **6**: a stirred toluene (100 mL) suspension of **5** (2.0 g, 1.5 mmol) was exposed to 1 atm of carbon monoxide for 30 h at room temperature. The white microcrystalline solid obtained was recrystallized from toluene (80%). Anal. Calcd for $C_{74}H_{98}K_2N_8O_2Zr_2$: C, 63.78; H, 7.04; N, 8.04. Found: C, 63.16; H, 7.10; N, 7.82. ^1H NMR (C_6D_6, room temperature): δ 7.60–6.80 (m, 3 H, C_5H_3N), 6.42–5.52 (m, 6 H, C_4H_2N), 2.62–1.65 (m, 16 H, CH_2), 1.40–0.50 (m, 24 H, Me). IR: $\nu_{Zr=O}$ (Nujol) 780.

(5) Crystal data for **6**: $C_{74}H_{98}K_2N_8O_2Zr_2$, $M = 1392.3$, triclinic, space group $P1$, $a = 12.508(3)$ Å, $b = 13.110(2)$ Å, $c = 12.130(3)$ Å, $\alpha = 98.70(2)°$, $\beta = 106.57(2)°$, $\gamma = 109.33(1)°$, $V = 1731.4(7)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.355$ g cm^{-3}; Mo Kα radiation ($\lambda = 0.710\,69$ Å) μ(Mo Kα) = 4.64 cm^{-1}; crystal dimensions 0.20 × 0.25 × 0.30 mm^3. The structure was solved by the heavy atom method (Patterson and Fourier synthesis) and anistropically refined by full-matrix least-squares for non-H atoms. For 4173 unique observed structure amplitudes $[I > 2\sigma(I)]$ collected at room temperature on a Rigaku AFC6S diffractometer in the range $5 < 2\theta < 50.1°$ and corrected for absorption, the R value is 0.036 ($R_w = 0.039$). The hydrogen atoms directly located from a ΔF map were introduced as fixed contributors prior the last stage of refinement ($U_{iso} = 0.08$ Å^2).

(6) K···C30′, 3.121(5); K···H301′, 2.60; K···H302′, 2.84; K···C34′, 3.546(5); and K···H342′, 2.52 Å.

(7) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 779. (b) Fay, R. C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 3, Chapter 32. (c) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Ellis Horwood: Chichester, U.K., 1986; p 103. Zr–O Distances in $[\{\eta^5\text{-}C_5H_5)_2ZrX\}_2O]$, typically 1.95 Å, are substantially shorter than a Zr–O single bond [2.20 Å]. (d) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767. In the trinuclear complex $[\{\eta^5\text{-}C_5H_5)_2ZrO\}_3]$, the Zr–O bond lengths [1.950(6)–1.966(5) Å are similar to those in dinuclear complexes. (e) Unpublished results.

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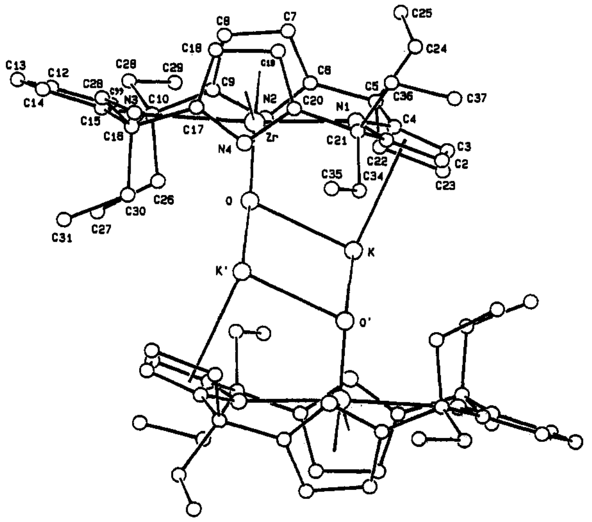

Figure 1. Perspective view (SCHAKAL) of **6**. Bond distances (Å) and angles (deg): Zr–O, 1.813(2); Zr-N1, 2.269(4); Zr-N3, 2.669(4); Zr-Cp2, 2.327(4); Zr-Cp4, 2.319(5); K-Cp1, 2.877(4); K-O, 2.607(3); K′-O, 2.611(3); N1-Zr-N3, 175.5(1); O-Zr-N3, 89.9(1); O-Zr-N1, 94.6(1); Cp2-Zr-Cp4, 133.1(1). Cp2 and Cp4 refer to the centroid of the pyrrolic rings containing N2 and N4, respectively. Non-hydrogen atoms are represented by isotropic spheres of arbitrary size for the purpose of clarity (′ = $-x$, $1 - y$, $-z$).

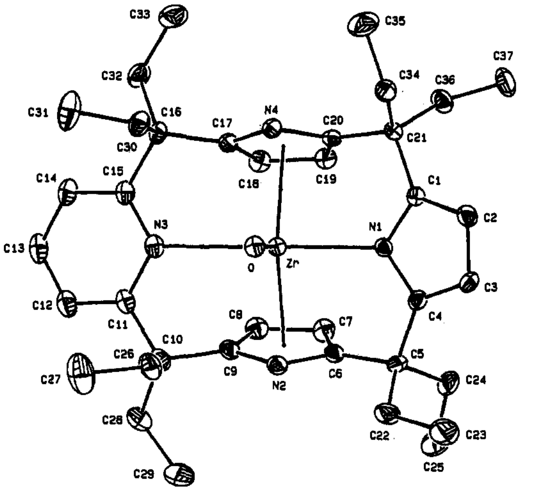

Figure 2. ORTEP drawing of the zirconyl unit in **6** (30% probability ellipsoids).

The formation of **6** requires the intermediacy of the carbenoid formyl group [A],[8] which adds to a C=C of one of the Zr-η^1-bonded pyrrolyl anions of the porphyrinogen.[9] This addition is followed by the cleavage of the C–O bond,[10] which is facilitated by the high oxophilicity of the metal. The geometrical proximity between the carbenoid formyl group and the pyrrolyl anion inhibits side reactions such as dimerization and reduction to formaldehyde.[8] According to the mechanism of homologation of pyrrole to pyridine by some carbene sources,[11] the carbon atom should be introduced in a meta position in the pyridine ring. This was confirmed by an important extension of reaction 3 in which complex **5** was reacted with ethylene and then exposed to carbon monoxide:

$$\mathbf{5} \xrightarrow{C_2H_4} \xrightarrow{CO} \underset{\mathbf{7}}{[\{\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_8(C_4H_2N)_3(3\text{-}EtC_3H_2N)Zr{=}O\}_2(\mu\text{-}K)_2]} \tag{4}$$

The insertion of ethylene into the Zr–H bond[2c] was followed by the carbonylation of the Zr–Et group. The resulting complex **7**,[12] found in 73% overall yield, contains, as confirmed by ^{1}H NMR and X-ray analysis, a 3-ethylpyridine residue. The hydrolysis of **6**[13] and **7**[14] gave the corresponding free ligands **2** and **3**.

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Supplementary Material Available: Tables of experimental details associated with data collection, fractional atomic coordinates, unrefined hydrogen coordinates, thermal parameters, and bond distances and angles for complex **6** (7 pages); listing of observed and calculated structure factors for complexes **5** and **6** (26 pages). Ordering information is given on any current masthead page.

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(8) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059. Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. Headford, C. E. L.; Roper, W. R. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York 1986; Vol. 1, Chapter 8.

(9) An interesting analogy can be found in the conversion of cyclopentadienyl anion into an alkylbenzene during the carbonylation of $[(\eta^5\text{-}C_5H_5)_3UR]$: Villiers, C.; Adam, R.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1992**, 1555. Related transformations can be found in: De Boer, E. J. M.; De With, J. *J. Organomet. Chem.* **1987**, *320*, 289. Hessen, B.; Blenkers, J.; Teuben, J. H.; Helgesson, G.; Jagner, J. *Organometallics* **1989**, *8*, 2809. Meyer, T. Y.; Messerle, L. *J. Am. Chem. Soc.* **1990**, *112*, 4564.

(10) A carbon monoxide deoxygenation study has been reported by: Neithamer, D. R.; LaPointe, R. E.; Wheeler, R. A.; Richeson, D. S.; Van Duyne, G. D. Wolczanski, P. T. *J. Am. Chem. Soc.* **1989**, *111*, 9056 and references therein.

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

(12) Preparation of **7**: a toluene (50 mL) suspension of **5** (5.55 g, 4.15 mmol) was heated at 70 °C for 15 h under an ethylene atmosphere and then reacted with CO at room temperature with stirring for 4 h. The light yellow solution was then evaporated to dryness. The solid was recrystallized from a mixture of toluene and *n*-hexane (73%). Anal. Calcd for $C_{78}H_{106}K_2N_8O_2Zr_2$: C, 64.73; H, 7.33; N, 7.74. Found: C, 65.34; H, 7.67; N, 7.48. ^{1}H NMR (C_6D_6): δ 7.24 (d, 1 H, C_5H_2N), 6.96 (q, 1 H, C_5H_2N), 6.16 (t, 4 H, C_4H_2N), 5.91 (s, 2 H, C_4H_2N), 2.67–1.90 (m, 18 H, CH_2), 1.29–0.63 (m, 27 H, Me).

(13) Hydrolysis of **6**, preparation of **2**: a toluene (100 mL) suspension of 6 (5.65 g, 4.06 mmol) was treated with a 5% aqueous solution of HCl (30 mL) and then neutralized with K_2CO_3. The organic phase was separated and then dried over Na_2SO_4. The toluene was evaporated to dryness, and the residue was dissolved in *n*-pentane (100 mL). Evaporation of pentane to a very small volume gave a crystalline solid (92%). Anal. Calcd for $C_{37}H_{52}N_4$: C, 80.43; H, 9.42; N, 10.14. Found: C, 80.46; H, 9.70; N, 10.02. ^{1}H NMR (CD_2Cl_2): δ 7.57 (t, 1 H, C_5H_3N), 7.20 (s, 1 H, NH), 7.18 (d, 2 H, C_5H_3N), 6.78 (s, 2 H, NH), 5.87 (t, 6 H, C_4H_2N), 2.18 (q, 4 H, CH_2), 2.02 (9, 4 H, CH_2), 1.76 (q, 4 H, CH_2), 1.75 (q, 4 H, CH_2), 0.63 (t, 12 H, Me), 0.58 (t, 12 H, Me).

(14) The hydrolysis of **7** was carried out in the same manner as for 6, yielding **3** (71%). Anal. Calcd for $C_{39}H_{56}N_4$: C, 80.69; H, 9.66; N, 9.66. Found: C, 80.45; H, 9.81; N, 9.53. ^{1}H NMR (CD_2Cl_2): δ 7.36 (d, 1 H, C_5H_2N), 7.34 (s, 1 H, NH), 7.13 (d, 1 H, C_5H_2N), 6.50 (s, 1 H, NH), 6.10 (s, 1 H, NH), 5.94 (m, 2 H, C_4H_2N), 5.86 (q, 2 H, C_4H_2N), 5.77 (m, 2 H, C_4H_2N), 2.29 (m, 4 H, CH_2), 2.04 (m, 4 H, CH_2), 1.72 (m, 10 H, CH_2), 0.95 (t, 3 H, Me), 0.69 (m, 6 H, Me), 0.58 (t, 6 H, Me), 0.57 (t, 6 H, Me), 0.39 (m, 6 H, Me).