Novel Reaction of *N*-Methyloctaethylporphyrinatocobalt(II) Acetate: Intramolecular Oxidative Alkylation

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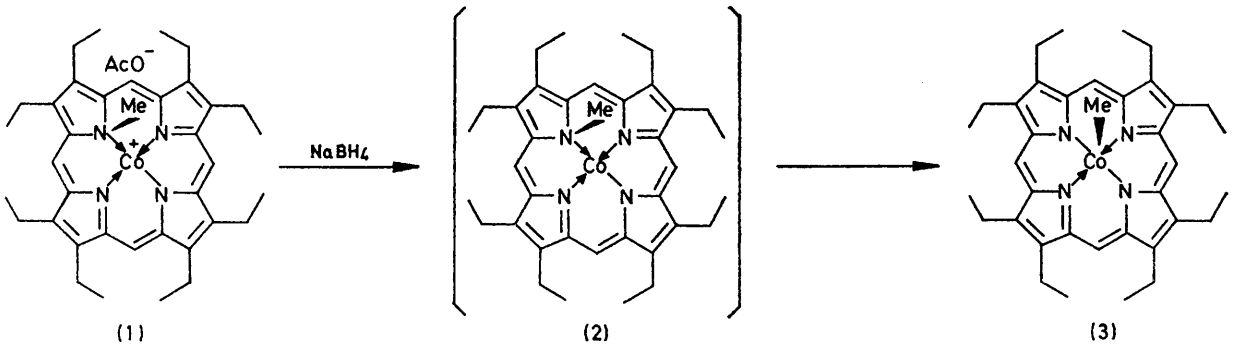
Summary Reduction of *N*-methyloctaethylporphyrinatocobalt(II) acetate with $NaBH_4$ generates methylcobalt(III)-octaethylporphyrin by a mechanism involving bond cleavage induced by the oxidation of Co^{I} to Co^{III}.

IN order to examine further the mechanism which we have proposed[1] for the novel migration of an alkyl group in *N*-methyl dirhodium(I) porphyrins, we have investigated the reduction of the cobalt(II) complex of *N*-methyloctaethylporphyrin (**1**)[2] with $NaBH_4$. Recent investigators have observed that $NaBH_4$ reduces cobalt(III) in porphyrins to cobalt(I).[3] Complex (**1**) was prepared almost quantitatively in the usual manner.[4] It gave a satisfactory elemental analysis, and its i.r. spectrum (KBr disc) showed a strong band at 1615 cm^{-1} indicative of acetate ion. The visible spectrum in $CHCl_3$ showed maxima at 379 (shoulder), 428 (log ϵ, 4·80), 542 (3·77), 588 (3·92), and 628 (shoulder) nm, similar to those reported for *N*-methyloctaethylporphyrinatozinc(II) chloride.[5] At room temperature, the reaction of (**1**) with NaBH$_4$ proceeded to completion in 30 min in tetrahydrofuran under argon to give the trivalent cobalt complex (**3**). Complex (**3**) was separated by t.l.c. on silica gel, followed by recrystallization from ClCH$_2$CH$_2$Cl–light petroleum, yielding dark purple crystals in 58% yield. All experimental procedures were carried out in the dark whenever possible since the complex is susceptible to thermal and/or light-induced homolytic fission of the cobalt–carbon bond.[6] The visible spectrum in CHCl$_3$ showed three maxima at 393 (5·33), 519 (4·02), and 552 (4·37) nm which are typical for metalloporphyrins.[4] Conclusive evidence for the trivalent cobalt–methyl bond was provided by the ^{1}H n.m.r. spectrum in CDCl$_3$, showing well resolved signals at τ 8·12 (24H, t, CH$_2$*Me*), 6·00 (16H, quartet, C*H*$_2$Me), −0·08 (4H, s, =CH–), and 15·20 br (3H, singlet, Co-Me). Similar upfield shifts of the methyl signal due to the porphyrin ring current have been reported for methylrhodium(III)octaethylporphyrin[1] and methylcobalt(III)etioporphyrin[6] (τ 16·47 and 15·15 respectively). Complex (**3**) was also identical with the product obtained by the reaction of pyridinobromocobalt(III)octaethylporphyrin with methyllithium.[7]

The methyl migration proceeds *via* reduction of Co$^{\mathrm{II}}$ to Co$^{\mathrm{I}}$. The instability of the *N*-methyl-porphyrin-cobalt(I) complex (**2**) seems to induce cleavage of the *N*-methyl bond *via* nucleophilic attack of the Co$^{\mathrm{I}}$ along with the release of strain energy of the four-co-ordinate complex (**2**). This unusual reaction can be considered to be an intramolecular oxidative addition through the C–N bond to the Co$^{\mathrm{I}}$ ion.



(1) (2) (3)

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[1] H. Ogoshi, T. Omura, and Z. Yoshida, *J. Amer. Chem. Soc.*, 1973, **95**, 1666.

[2] W. K. McEwen, *J. Amer. Chem. Soc.*, 1946, **68**, 711.

[3] E. B. Fleischer and M. Krishnamurthy, *J. Amer. Chem. Soc.*, 1972, **94**, 1382; J. Chatt, C. M. Elson, and G. J. Leigh, *ibid.*, **1973**, **95**, 2408.

[4] J. E. Falk, 'Porphyrins and Metalloporphyrins,' Elsevier, Amsterdam, 1964.

[5] R. Grigg, G. Shelton, and A. Sweeney, *J.C.S. Perkin I*, 1972, 1789.

[6] D. A. Clarke, D. Dolphin, R. Grigg, A. W. Johnson, and H. A. Pinnock, *J. Chem. Soc.* (*C*), 1968, 881.

[7] H. Ogoshi, E. Watanabe, N. Koketsu, and Z. Yoshida, manuscript in preparation.