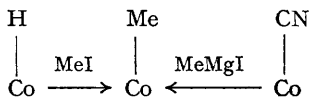


Alkyl-cobalt(III) Complexes of Aetioporphyrin I

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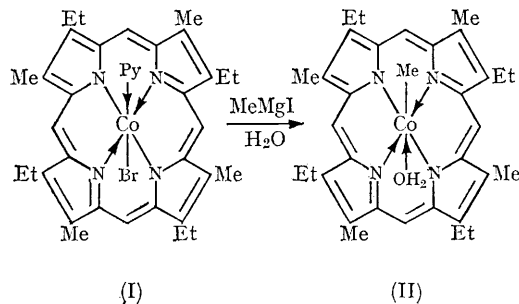
OCTAHEDRAL cobalt(III) alkyl complexes in the cobalamin series can be prepared in polar solvents by reaction of the reduced species, B_{12s} , which is possibly a hydride, with diazomethane or an alkyl halide, sulphate, toluene-*p*-sulphonate, *etc.*^{1,2} However, when the cobalamin complex (*e.g.* hepta-ethyl ester rather than hepta-amide) is soluble in ethereal solvents then the cobalt(III) species can be reacted with methylmagnesium iodide to yield the cobaltic methyl derivative.³



Both of these methods were used recently to prepare a series of cobalt(III) alkyl derivatives from cobalt(III) complexes of dimethylglyoxime.⁴ Attempts to prepare suitable cobalt complexes of porphyrins for reaction with alkyl halides by reduction of octahedral cobalt(III) porphyrin derivatives⁵ invariably led to the formation of the stable planar cobalt(II) complexes. However, methyl- (II) (71%) and ethyl-cobalt(III) (55%) aetioporphyrin I derivatives have now been obtained by reaction of the pyridinobromocobalt(III) complex (I) with alkylmagnesium halides in anhydrous 1,2-dimethoxyethane. The methyl- and ethyl-cobalt(III) complexes have been isolated as light-sensitive red prisms [λ_{max} (CHCl_3) of Me-Co^{III} complex: 266, 313, 391, 520, and 533 m μ ;

ϵ 21,000, 23,100, 229,000, 11,400, and 2700 respectively], and spectroscopic evidence has been obtained for the existence of the allyl-, cyclohexyl-, and phenyl-cobalt(III) analogues. The alkyl-cobalt derivatives (*e.g.* II) are neutral complexes; the lack of pyridine resonances in the n.m.r. spectrum and the presence of a sharp infrared band at 3670 cm^{-1} suggests that the pyridine ligand has been replaced by water during the reaction.

The n.m.r. spectrum of the methylcobalt complex (II) provides the main evidence for the assigned structure, as it includes a sharp singlet at τ 15.15, associated with the methyl group attached to the cobalt atom, and clearly under the influence of the ring current of the porphyrin macrocycle. (*cf.* ref. 6.) Similarly the spectrum of the ethylcobalt complex contained a triplet centred at τ 15.67, associated with the CH_3 of the ethyl group and a



¹ A. W. Johnson, L. Mervyn, N. Shaw, and E. Lester Smith, *Nature*, 1962, **194**, 1175; *J. Chem. Soc.*, 1963, 4146; E. Lester Smith, L. Mervyn, P. W. Muggleton, A. W. Johnson, and N. Shaw, *Ann. New York Acad. Sci.*, 1964, **112**, 565.

² K. Bernhauer, O. Müller, and G. Müller, *Biochem. Z.*, 1962, **336**, 102; O. Müller and G. Müller, *ibid.*, p. 299; O. Müller and K. Bernhauer, *Ann. New York Acad. Sci.*, 1964, **112**, 575.

³ F. Wagner and K. Bernhauer, *Ann. New York Acad. Sci.*, 1964, **112**, 580.

⁴ G. N. Schrauzer and J. Kohnle, *Chem. Ber.*, 1964, **97**, 3056.

⁵ A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 1960, 2979.

⁶ F. Sondheimer, *Pure Appl. Chem.*, 1964, **7**, 363; Y. Gaoni and F. Sondheimer, *J. Amer. Chem. Soc.*, 1964, **86**, 521.

poorly resolved quartet centred at $\tau 15.24$ associated with the CH_2 of the ethyl group. Singlets at $\tau 0.10$ in the methyl- and at $\tau 0.23$ in the ethyl-cobalt(III) complex corresponded to the four *meso*-protons in each case. The signals associated with the β -alkyl groups on the periphery of the macrocycle were unequivocal. In the n.m.r. spectrum of the original pyridinobromocobalt(III) complex (I), the high-field signals at $\tau 15-16$ were absent and it was of interest to note that the absorptions associated with the protons of the pyridine ring were at abnormally high values, again due to the

influence of the porphyrin ring current⁷ (α -protons, signal centred about $\tau 4.77$; β -protons about $\tau 5.8$ and γ -proton about $\tau 5.6$).

Like the alkylcobalamins,⁸ solutions of the alkylcobalt(III) aetioporphyryns were stable towards potassium cyanide in the absence of light, but in daylight the alkyl-metal bond was rapidly photolysed and potassium [aetioporphyryn I dicyanocobaltate(III)]⁵ was obtained. Further reactions of the alkylcobalt(III) porphyrin complexes are under investigation.

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⁷ C. B. Storm and A. H. Corwin, *J. Org. Chem.*, 1964, **29**, 3700.

⁸ D. Dolphin, A. W. Johnson, and R. Rodrigo, *J. Chem. Soc.*, 1964, 3186; D. Dolphin, A. W. Johnson, R. Rodrigo, and N. Shaw, *Pure Appl. Chem.*, 1963, **7**, 539.