

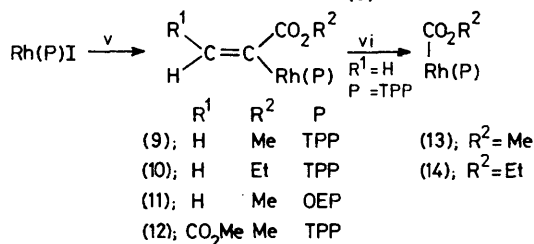
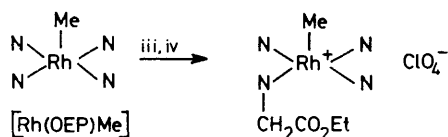
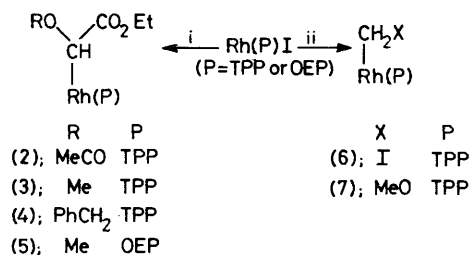
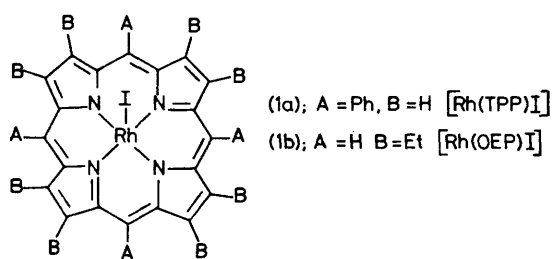
Alkyrhodium(III) Porphyrins from Rhodium(III) Porphyrins and Diazoalkanes

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Summary Reaction of Rh^{III} porphyrins with diazoalkanes leads to the formation of metal-alkylated products; significant differences from the corresponding Co^{III} series are noted, *e.g.*, catalytic decomposition of the reagents and fragmentation of primary olefinic products to give Rh(CO₂R) porphyrins.

ALKYLCOBALT and alkyrhodium porphyrins have been studied as models for alkylcobalt corrins. Alkyrhodium porphyrins were recently obtained *via* alkylation of, or oxidative addition on various Rh^I,^{1,2} dimeric Rh^{II},³ hydrido-Rh^{III},⁴ or carbonyl-Rh^{III} porphyrins.⁵ We have demonstrated that the reaction of various diazo derivatives with Co^{III} porphyrins leads to high yields of alkylcobalt-



i, N₂CHCO₂Et, ROH; ii, CH₂N₂, MeOH; iii, N₂CHCO₂Et, MeCO₂H; iv, NaClO₄; v, R¹CH₂C(N₂)CO₂R²; vi, excess of reagent v. TPP = Tetraphenylporphyrin; OEP = octaethylporphyrin.

† RhOEPI and RhTPPI (up to 90% yield) were prepared according to the procedure described in ref. 2a.

‡ All products have been fully characterized by elemental analysis, n.m.r., i.r., visible, and mass spectra. Yields are not optimized and are calculated with respect to the porphyrinic starting material.

§ These intermediates could be isolated (see A. W. Johnson, D. Ward, P. Batten, A. L. Hamilton, G. Shelton, and C. M. Elson, *J.C.S. Perkin I*, 1975, 2076; A. W. Johnson and D. Ward, *ibid.*, 1977, 720) or only detected as intermediates (see ref. 6).

¹ H. Ogoshi, J. Setsune, T. Omura, and Z. Yoshida, *J. Amer. Chem. Soc.*, 1975, **97**, 6461; B. R. James and D. V. Stynes, *J.C.S. Chem. Comm.*, 1972, 1261.

² (a) A. M. Abeysekera, R. Grigg, J. Trocha-Grimshaw, and V. Viswanatha, *J.C.S. Perkin I*, 1977, 36, 1395; (b) H. Ogoshi, T. Omura, and Z. Yoshida, *J. Amer. Chem. Soc.*, 1973, **95**, 1666.

³ H. Ogoshi, J. Setsune, and Z. Yoshida, *J. Amer. Chem. Soc.*, 1977, **99**, 3869.

⁴ Z. Yoshida and H. Ogoshi, Japan Kokai 77 59,199 and 77 59,200 (*Chem. Abs.*, 1977, **87**, 152290, 184561).

⁵ I. A. Cohen and B. C. Chow, *Inorg. Chem.*, 1974, **13**, 488.

⁶ H. J. Callot and E. Schaeffer, *Tetrahedron Letters*, 1977, 239; *J. Organometallic Chem.*, 1978, **145**, 91.

(iii) porphyrins⁶ and hoped to extend the method to Rh complexes.

Reaction of ethyl diazoacetate with Rh^{III} tetraphenylporphyrin iodide [Rh(TPP)I][†] (1a) in the presence of MeOH, PhCH₂OH, or MeCO₂H led to alkylrhodium(III) porphyrins (2) (56%), (3) (16%), and (4) (47%).[‡] Similarly, reaction with CH₂N₂ gave either (6) (47%), or a mixture of (6) (6%) and (7) (35%) (in the presence of MeOH). Rhodium(III) octaethylporphyrin iodide [Rh(OEP)I] (1b) likewise gave the alkylrhodium porphyrin (5) (69%) on treatment with ethyl diazoacetate and methanol. A possible intermediate, in which a carbene would be inserted between the metal and a ring nitrogen atom, as in the cobalt series,[§] could not be detected. However the reaction of methylrhodium(III)-OEP with ethyl diazoacetate and acetic acid under similar conditions gave the salt (8) (90%) which crystallized as the perchlorate; a similar salt was obtained in the TPP series but could not be isolated in a pure state. These facts demonstrate that, although compounds (2)–(7) may arise from addition on an intermediate Rh-carbene species, an interaction with the ring nitrogens cannot be excluded [in (8) the methyl and CH₂CO₂Et groups have been arbitrarily placed on the opposite faces of the macrocycle].

Diazo esters possessing a β-hydrogen atom (diazopropionic or succinic esters) also react with Rh^{III} porphyrins to yield olefins (9) (30%), (10) (30%), (11) (36%), and (12) (47%) as expected, based on observations in the cobalt series. However, both the reaction conditions and the further course of the reaction in the two systems are different. Firstly, decomposition of the diazoester competes efficiently with the formation of the alkylrhodium compound, thus decreasing the yields. Secondly, the olefins (9) and (10) are unstable in the presence of an excess of reagent since compounds (13) and (14)⁵ slowly form at their expense. Experiments starting with (9) or (10) and using methyl or ethyl diazopropionate as reagent proved that the ester group in (13) or (14) originates in the diazo ester and not the olefin.

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