Oxidative Addition Reactions of Dirhodium(I) Complexes of Porphyrins

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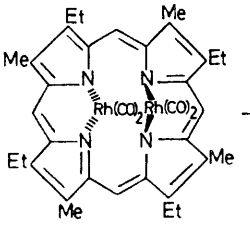
Summary Oxidative addition reactions of dirhodium(I) complexes of porphyrins provide an efficient route to acyl- and alkyl-Rh^{III} porphyrins.

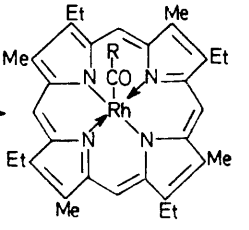
THE unusual chemistry of vitamin B_{12} coenzyme has stimulated interest in the related cobalt[1] and rhodium[2] porphyrins. Rhodium(I) porphyrins are of particular interest because of the greater stability of rhodium(I) complexes compared to cobalt(I) complexes. We have recently developed an improved method for the synthesis of dirhodium(I) complexes of porphyrins[3] and these have now been found to undergo a range of oxidative addition reactions.

The acylrhodium(III) complexes (**2**; R = Me, Et, or Pr^n) are formed in good yield (82—92%)† by heating a $CHCl_3$ solution of (**1**) with an excess of the appropriate carboxylic acid anhydride. There is an induction period of up to 3 h for these reactions. Maximum shielding in the n.m.r. spectrum of (**2**) occurs for the protons attached to the carbon adjacent to the carbonyl group, *i.e.* the β-carbon atom. The n.m.r. signals for the terminal methyl groups in (**2**; R = Me, Et, or Pr^n) occur at τ 13·90, 12·23, and 11·63 respectively. In contrast to other unsymmetrical porphyrins[3] the *meso*-acetoxyporphyrin (**3**) forms a single dirhodium complex analogous to (**1**), whereas the azaporphyrin (**4**) gives a mixture of dirhodium(I) complexes. The dirhodium complexes of (**3**) and (**4**) also undergo oxidative addition. When (**1**) or the dirhodium complex of (**3**) are heated in boiling Ac_2O a mixture of the corresponding methyl- and acetyl-Rh^{III} complexes are obtained. Thus (**1**) after 1 h in boiling Ac_2O gives (**2**; R = Me; 67%) and (**5a**; 21%). Both methyl and acetyl derivatives are obtained from oxidative additions with MeI.[3]

The dirhodium(I) porphyrin complexes also react with cyclopropanes. When (**1**) was heated with cyclopropyl 4-fluorophenyl ketone at 110 °C ring opening occurred to give (**5b**; 32%). The n.m.r. spectrum of (**5b**) showed signals for the *p*-fluorophenyl protons centred at τ 3·3. The protons of the trimethylene chain attached to rhodium gave rise to multiplets centred at τ 16·15, 14·90, and 11·18. Heating (**1**) with cyclopropyl methyl ketone at 110 °C for 20 h did not lead to ring opening but gave the cyclopropyl



(1)



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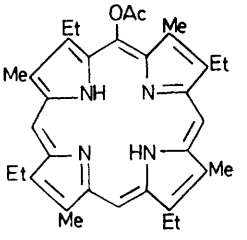

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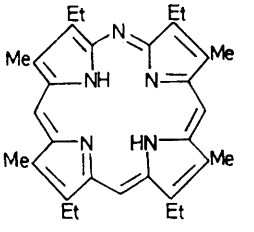

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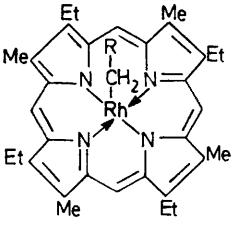

(5)

a; R = H
b; R = $[CH_2]_2COC_6H_4F$
c; R = CO—△
d; R = $[CH_2]_2COMe$
e; R = COPh

† Satisfactory analytical and spectral data have been obtained for all new compounds.

ketone complex (**5c**; 83%). The methylene group attached to rhodium gave rise to a doublet in the n.m.r. spectrum, centred at τ 16·05 (J_{Rh-H} 4·3 Hz). The signals for the cyclopropyl group occurred as multiplets at τ 14·10 (1H), 11·64 (2H), and 11·20 (2H). Whilst our work was in progress the reaction of rhodium(I) octaethylporphyrin with cyclopropyl ketone to give (**5d**) was reported.[4]

The major reason for the difference in products from the reaction of (**1**), or of rhodium(I) octaethylporphyrin, with cyclopropyl methyl ketone is that in the latter case a negatively charged (more nucleophilic) rhodium complex is involved whilst in our case a neutral rhodium(I) species is used. No reaction occurred when rhodium(III) etioporphyrin acetate was heated with cyclopropyl methyl ketone thus ruling out nucleophilic attack of the ketone enolate on an intermediate Rh^{III} porphyrin. Thus (**5c**) arises formally from an oxidative addition of the C–H bond of a methyl ketone‡ to Rh^{I} followed by collapse of the Rh^{III} species into the centre of the porphyrin ring. The reaction appears quite general for ketones.

Thus acetophenone (120 °C, 4 h) gives (**5e**; 45%) and ethyl phenyl ketone (120 °C, 5 h) gives the corresponding RhCH(Me)C(O)Ph complex (23%). Products, as yet uncharacterised have been obtained from dialkyl ketones, other active methylene compounds, and aldehydes.§

Aryl- and aroyl-Rh^{III} complexes can also be prepared from appropriate precursors. Thus (**1**) and benzoyl chloride (110 °C, 1 h) give (**2**; R = Ph; 82%), whilst (**1**) and benzoic anhydride (110 °C, 3 h) give a mixture of (**2**; R = Ph; 29%) and the corresponding Rh–Ph complex (27%). The phenyl-Rh^{III} complex has been obtained recently by a different route.[2] In the reported n.m.r. spectrum of this complex the *ortho*-protons of the phenyl group were not located. We observe these protons as a doublet centred at τ 10·38 ($CDCl_3$).

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‡ A π-complexed enol appears an attractive intermediate.

§ Other oxidative additions including further examples of cyclopropanes are currently being studied.

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