Dicarbonylrhodium(I) Complexes of Polypyrrole Macrocycles. Part 1. Preparation and Oxidative Addition Reactions with Alkyl Halides and Carboxylic Acid Anhydrides

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The reaction of polypyrrole macrocycles with di-μ-chloro-bisdicarbonylrhodium gives rise to out-of-plane mono- (with corroles and thiaphlorins) or bis-dicarbonylrhodium (with porphyrins and azaporphyrins) complexes, depending on the number of imino- and amino-groups present in the central macrocycle cavity. The tautomeric oxophlorins give both mono- and bis-dicarbonylrhodium complexes and the cobalt(III) complex of aetio-oxophlorin is shown by n.m.r. to exist as the aromatic zwitterion in benzene solution. The dicarbonylrhodium(I) complexes undergo oxidative addition reactions with alkyl halides and carboxylic acid anhydrides to give the corresponding alkyl- and acyl-rhodium(III) complexes of the polypyrrole macrocycles.

METALLOPORPHYRINS containing central metal atoms capable of redox reactions (*e.g.* Fe and Co) have attracted interest because of their relationship to the naturally occurring porphyrin redox systems, the haemoproteins, and, more indirectly, vitamin B_{12} coenzyme. We had previously prepared various iron(III) and cobalt(III) alkyl-, aryl-, and acyl-metalloporphyrins (1; M = Fe^{III} or Co^{III}),[1] and had briefly studied some reactions of the cobalt complexes. A study of the corresponding rhodium complexes was undertaken because the expected greater stability of the rhodium complexes would permit a more detailed investigation of their chemistry.

Rhodium complexes of porphyrins have attracted increasing interest in recent years and complexes of Rh^{I},[2,3] Rh^{II},[2] and Rh^{III} [4] have been reported. Studies on the ' in-plane ' Rh^{I} complexes [3] have confirmed their expected nucleophilic character and alkylation with alkyl halides,[3] Michael addition to electronegative olefins and alkynes,[3] and nucleophilic attack on dimethylacetamide [5] have provided routes to a range of interesting alkyl-, alkenyl-, and (in the last case) acetylrhodium(III) porphyrin complexes. Rhodium(III) complexes of porphyrins also react with organolithium compounds to give the appropriate organorhodium(III) porphyrin complexes.[3] The rhodium carbonyl complex (2) undergoes nucleophilic attack (by OEt^- or NEt_2^-) at the co-ordinated carbonyl group, giving (3; R = OEt or NEt_2) in good yield.[6]

The methods devised by previous workers for generating organorhodium(III) porphyrins suffer from several disadvantages. Routes employing ' in-plane ' rhodium(I) complexes involve reduction of the corresponding rhodium(III) porphyrins, which are themselves obtained by conventional methods [4] in only moderate yield. Secondly the ' in-plane ' rhodium(I) complexes are air-sensitive and need to be generated and trapped *in situ*. We were attracted to the possibility that the previously described air-stable dirhodium(I) complex (4; R = Et) might prove a direct precursor of organorhodium(III) porphyrins by suitable oxidative addition reactions.

The reported synthesis of (4; R = Et) [3] gives the complex in poor yield in comparison with the very high yields obtained in the majority of metal complexation reactions of porphyrins. A modification of the previous method, involving adding a solution of di-μ-chloro-bisdicarbonylrhodium in chloroform to a solution of the porphyrin in chloroform containing an excess of anhydrous sodium acetate, gives the complexes in high yield [*e.g.* (4; R = Me), 89%; (4; R = Et), 98%].[7] Reactions in the absence of added buffering agent are slower and proceed less cleanly. Deuteroporphyrin IX (5a) and protoporphyrin IX (5b) also give analogous complexes in 88 and 97% yield, respectively. The dirhodium complexes derived from unsymmetrical porphyrins [*e.g.* (5a and b)] and the azaporphyrin (6;

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

[2] B. R. James and D. V. Stynes, *J. Amer. Chem. Soc.*, 1972, **94**, 6225.

[3] H. Ogoshi, T. Omura, and Z. Yoshida, *J. Amer. Chem. Soc.*, 1973, **95**, 1666; H. Ogoshi, J.-I. Setsune, T. Omura, and Z.-I. Yoshida, *ibid.*, 1975, **97**, 6461.

[4] N. Sadasivan and E. B. Fleischer, *J. Inorg. Nuclear Chem.*, 1968, **30**, 591.

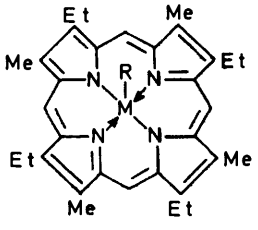
[5] B. R. James and D. V. Stynes, *J.C.S. Chem. Comm.*, 1972, 1261.

[6] I. A. Cohen and B. C. Chow, *Inorg. Chem.*, 1974, **13**, 488.

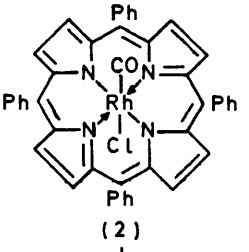
[7] Preliminary communications, R. Grigg, J. Trocha-Grimshaw, and V. Viswanatha, *Tetrahedron Letters*, 1976, 289; A. M. Abeysekera, R. Grigg, J. Trocha-Grimshaw, and V. Viswanatha, *J.C.S. Chem. Comm.*, 1976, 227.

X = N, $R^1 = R^2 = R^4$ = Et, $R^3 = R^5$ = Me) are mixtures of two isomers, as demonstrated by their n.m.r. spectra. Interestingly the unsymmetrical *meso*-acetoxyporphyrin (6; X = C·OAc, $R^1 = R^3 = R^5$ = Et, $R^2 = R^4$ = Me) gives a single dirhodium complex. The reaction is not limited to porphyrins: both corroles [*e.g.* (7)] and the *meso*-thiaphlorin (8) [8] give monodicarbonylrhodium(I) complexes, in 36 and 76% yield, respectively.

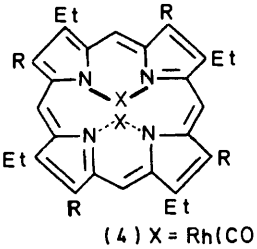
The formation of monorhodium complexes by (7) and (8) is clearly the result of the presence of only one imine-type nitrogen atom in each macrocycle. Each co-ordinated dicarbonylrhodium unit requires the presence



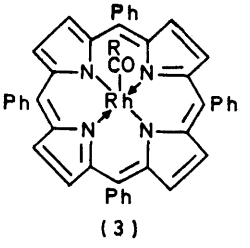
(1)



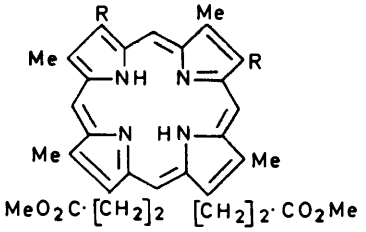
(2)



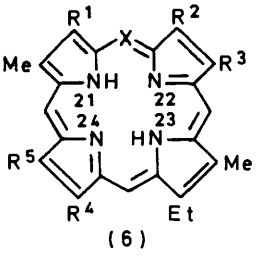
(4) X = $Rh(CO)_2$



(3)



(5) a; R = H
b; R = CH:CH_2



(6)

of one NH group and one imine nitrogen atom. The macrocycles (7) and (8) are each capable of forming four monorhodium complexes, since the inner pyrrolic hydrogen atoms are subject to tautomeric shifts, *e.g.* in (8) the dicarbonylrhodium unit could bridge positions 21 and 22, 23 and 24, 22 and 23, or 21 and 23. Bridging between positions 21 and 22 or 23 and 24 would give rise to a symmetrical n.m.r. spectrum, but the unsymmetrical nature of the spectra of the monorhodium complexes of (7) and (8) rule out such symmetrical structures. It is not possible to distinguish unequivocally between the 21,23- and the 22,23-bridging arrangements. However the 22,23-structure is favoured

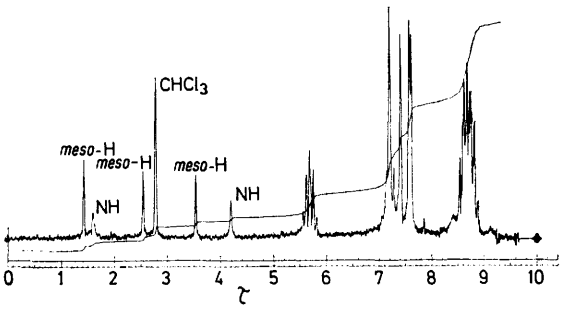
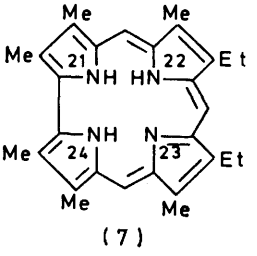
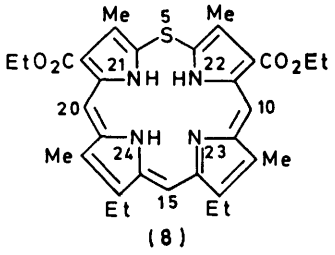


FIGURE 1 N.m.r. spectrum of the dicarbonylrhodium complex (10) of a *meso*-thiaphlorin

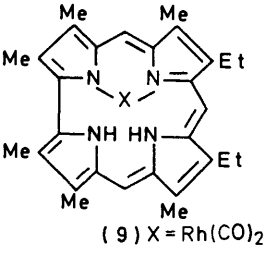
by analogy with the structures of the dirhodium complexes [*e.g.* (4)] [9] and, perhaps less persuasively, by the observation that porphyrins undergo di-*N*-alkylation on adjacent rings (22,23) rather than at positions 21 and 23.[10] Corroles are also thought to undergo di-*N*-alkylation at adjacent positions (21 and 22).[11] The monorhodium complexes are therefore formulated as (9) and (10), respectively. The n.m.r. spectrum of (10) (Figure 1) shows a marked downfield shift of one of the *meso*-proton signals to τ 1.40. The parent macrocycle (8) exhibits *meso*-proton signals at τ 2.48 (2 H) and 3.73 (1 H), which suggests that it is one of two equivalent (10 or 20) *meso*-protons of (8) that has suffered a large downfield shift in (10), and this accords with the 22,23-bridged formulation (10). The presence of low-field imino-proton signals (Figure 1) confirms that the



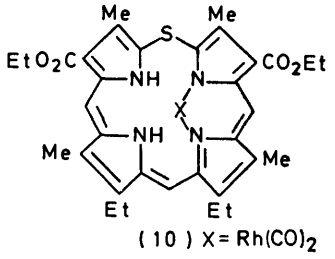
(7)



(8)



(9) X = $Rh(CO)_2$



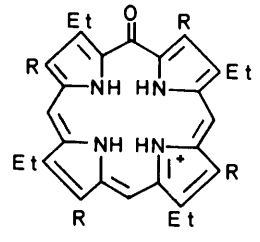
(10) X = $Rh(CO)_2$

thiaphlorin oxidation level is unchanged. The mono- are less stable than the bis-dicarbonylrhodium complexes; both (9) and (10) undergo extensive decomposition on crystallisation.

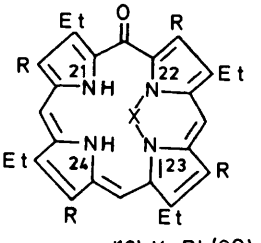
[8] M. J. Broadhurst, R. Grigg, and A. W. Johnson, *J.C.S. Perkin I*, 1972, 1124.
[9] A. Takenaka, Y. Sasada, H. Ogoshi, T. Omura, and Z. Yoshida, *Acta Cryst.*, 1975, **31B**, 1.
[10] R. Grigg, G. Shelton, A. Sweeney, and A. W. Johnson, *J.C.S. Perkin I*, 1972, 1789.
[11] M. J. Broadhurst, R. Grigg, A. W. Johnson, and G. Shelton, *J.C.S. Perkin I*, 1972, 143.

The requirements of one imino- and one amino-nitrogen atom for complexation of each dicarbonylrhodium unit suggested that the potentially tautomeric oxophlorins might form both mono- and bis-dicarbonylrhodium complexes. The oxophlorin (6; keto tautomer of X = C·OH, $R^1 = R^3 = R^5 = Et$, $R^2 = R^4 = Me$) and octaethyloxophlorin each give two isolable complexes one of which (green) is a mono- and the other (red) a bis-dicarbonylrhodium complex. However, t.l.c. and n.m.r. studies show that a complicated series of reactions is occurring, and the amounts of the green and the red products are variable. This variability is related to the known instability of oxophlorins [12-15] and their tendency to form radical species and undergo oxidation.[14,15]

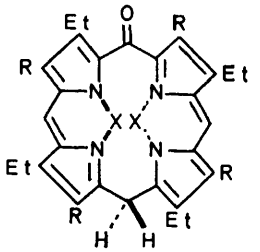
The red complex, which contained two dicarbonylrhodium groups, was stable and could be crystallised from chloroform. The green complex contained only one dicarbonylrhodium unit and decomposed on attempted crystallisation. The green complexes have a pattern of i.r. bands at 1 500—1 600 cm^{-1} similar to that of the parent oxophlorins, and their electronic spectra (Figure 2) resemble that of an oxophlorin monocation (11; R = Me or Et).[12] This suggests that the complexes have structure (12; R = Me or Et), analogous to the *meso*-thiaphlorin complex (10). Bridging of the dicarbonylrhodium between positions 21 and 22 or 23 and 24 cannot be ruled out. Indeed, the n.m.r.



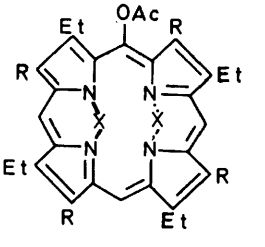
(11)



(12) X = $Rh(CO)_2$



(13) X = $Rh(CO)_2$



(14) X = $Rh(CO)_2$

spectrum of (12; R = Me) (or its isomers) shows, by the number of signals in the *meso*-proton region, that in solution ($CDCl_3$) it is a mixture.

The less polar, red complex exhibits a much stronger carbonyl i.r. band (at *ca.* 1 600 cm^{-1}) than either the oxophlorins or the green complexes. The electronic spectrum (Figure 2) is typical of a blocked chromophore

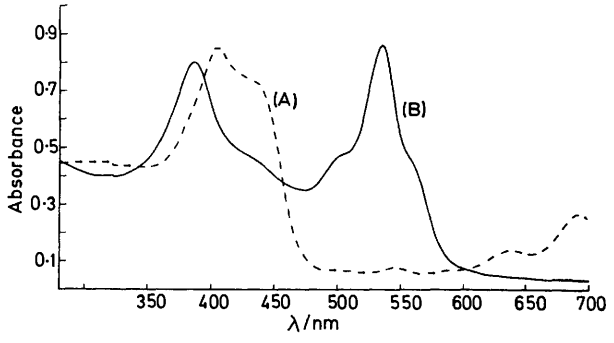


FIGURE 2 Electronic spectra of *ca.* 2.4 × 10^{-6}M-solutions in chloroform of (A) mono- and (B) bis-dicarbonylrhodium complexes of aetio-oxophlorin

and resembles that of a dipyrromethene. The red complex proved paramagnetic in solution and it was not possible to determine its n.m.r. spectrum. We tentatively formulate the dirhodium(I) complex as (13; R = Me or Et).* The bisdicarbonylrhodium complex of the *meso*-acetoxyporphyrin (6; X = C·OAc, $R^1 = R^3 = R^5 = Et$, $R^2 = R^4 = Me$) is partially converted (9%) into the red complex formulated as (13; R = Me) when it is chromatographed on alumina. Comparison of the n.m.r. spectra of the *meso*-acetoxyporphyrin (6; X = C·OAc, $R^1 = R^3 = R^5 = Et$, $R^2 = R^4 = Me$) and its bisdicarbonylrhodium complex shows a downfield shift of the two-proton *meso*-signal from τ −0.06 to −0.27, whereas the one-proton *meso*-signal is essentially unchanged (τ 0.10 and 0.12, respectively), which is slight evidence for preferring (14) as the structure of the complex.

N.m.r. spectra of oxophlorins and their metal complexes are invariably broad and ill-defined owing to the formation of paramagnetic species. As part of our work associated with the oxophlorin–di-μ-chloro-bisdicarbonylrhodium system we prepared dipyridinecobalt(III) aetio-oxophlorin for comparison. The related dipyridinecobalt(III) octaethyloxophlorin is reported to give broad n.m.r. spectra in both chloroform and pyridine.[16] We also obtained broad spectra in chloroform but were able to obtain a sharp n.m.r. spectrum (Figure 3) in degassed hexadeuteriobenzene. The signals for the protons of the co-ordinated pyridines occur at *ca.* τ 4.8 [C(4) protons] and the signals for the more shielded C(2) and C(3) protons are obscured by the signals of the macrocycle (Figure 3). The strong shielding of the pyridine protons demonstrates that in

* Alternative bridging structures and protonation sites cannot be ruled out, but structure (13) would offer the greatest relief of strain, and the *meso*-position opposite the *meso*-oxy-substituent is the site of electrophilic reactions in oxophlorins. Further work, including n.m.r. studies in degassed solvents is under way to try to unravel the complex situation found for oxophlorins.

[12] A. H. Jackson, G. W. Kenner, and K. M. Smith, *J. Chem. Soc.* (*C*), 1968, 302.
[13] R. Bonnett, M. J. Dimsdale, and G. F. Stephenson, *J. Chem. Soc.* (*C*), 1969, 564.
[14] J.-H. Furhop, S. Besecke, J. Subramanian, C. Mengersen, and D. Risner, *J. Amer. Chem. Soc.*, 1975, **97**, 7141.
[15] G. H. Barnett, B. Evans, and K. M. Smith, *Tetrahedron*, 1975, **31**, 2711.
[16] R. Bonnett and M. J. Dimsdale, *J.C.S. Perkin I*, 1972, 2540.

hexadeuteriobenzene the complex exists in the aromatic zwitterionic form (Figure 3) rather than the non-aromatic neutral oxophlorin form. A detailed study of the oxidation potentials of metallo-oxophlorins, which is reported to be in progress,[14] may further clarify the effect of solvent and metal ion.

Some observations on the mechanism of formation of complexes of the type (4) have been made. Thus, it is reported that prolonged boiling of a solution of octaethylporphin and di-μ-chloro-bisdicarbonylrhodium in chloroform gives the porphyrin salt (15; R = Et).[17] A recent review [18] proposes that (15) is an intermediate in the formation of (4; R = Et) and incorrectly ascribes this suggestion to Cetinkaya *et al.*[17] We have studied the reaction of aetioporphyrin I with di-μ-chloro-bisdicarbonylrhodium in both cold and hot chloroform; t.l.c. shows that in both cases the complex (4; R = Me) is formed initially and is then slowly converted into several other products including (15; R = Me). However (15; R = Me) does react with sodium acetate to form (4; R = Me). Reactions carried out in benzene or chloroform, with or without sodium acetate, and with varying amounts of di-μ-chloro-bisdicarbonylrhodium (from 0.5 mol. equiv. upwards) show no evidence of formation of an intermediate monorhodium(I) complex (16) with aetioporphyrin I or octaethylporphyrin. These observations are open to several interpretations. The porphyrin may form a complex with 2 mol. equiv. of reagent by stepwise *trans*-co-ordination *via* the imine nitrogen atoms followed by cleavage of the chloro-bridges and conversion into product. These reactions involving 16- and 18-electron rhodium species would be expected to occur readily. Co-ordination of intact di-μ-chloro-bisdicarbonylrhodium to an *N*-alkylporphyrin

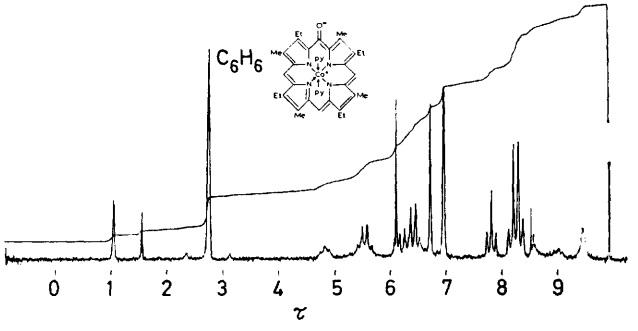
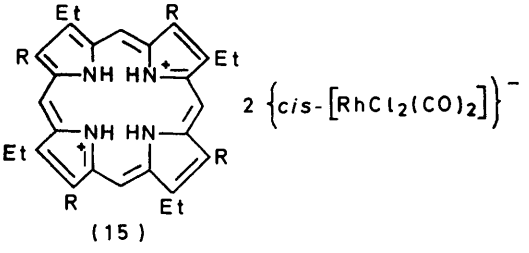


FIGURE 3 N.m.r. spectrum of dipyridinecobalt(III) *meso*-hydroxyaetioporphyrin zwitterion in degassed C_6D_6

giving (17) [3] has been reported. An alternative stepwise co-ordination of the two dicarbonylrhodium units to the porphyrins *via* chloro-bridge splitting, might occur with a faster co-ordination of the second dicarbonylrhodium than the first. *N*-Alkylation is known to increase the basicity of pyrrolic nitrogens in porphyrins and corroles,[19] and ' out-of-plane ' co-ordination to a low-valent transition metal ion might have a similar effect. The released acid, $H[Rh(CO)_2Cl_2]$, is neutralised by the buffering agent (Na_2CO_3 or NaOAc).



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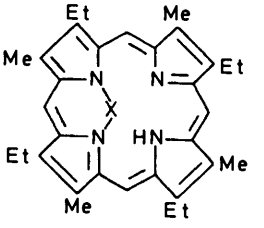
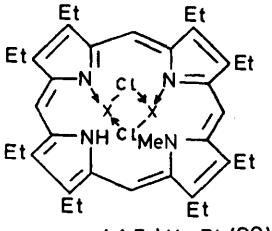


(16) X = $Rh(CO)_2$



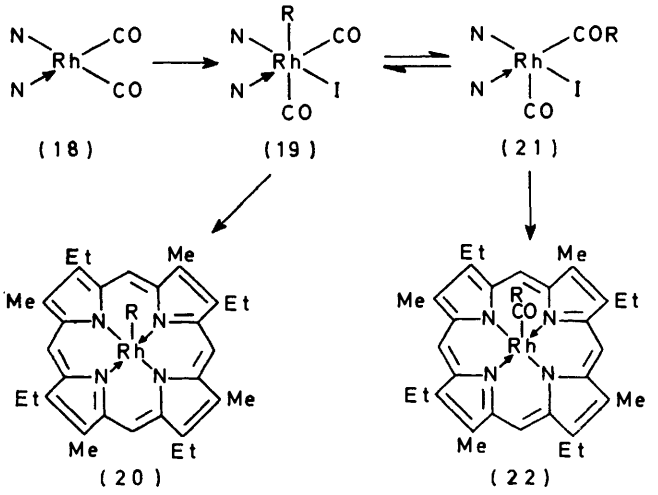
(17) X = $Rh(CO)_2$

The various mono- and bis-dicarbonylrhodium complexes of polypyrrole macrocycles undergo a range of oxidative addition reactions. Thus (4; R = Me) reacts with methyl iodide at room temperature over 4 days to give a mixture of methyl- and acetyl-rhodium(III) porphyrins (20; R = Me) and (22; R = Me) in the ratio 8 : 11, and trideuteriomethyl iodide gives the corresponding deuteriated products. Ethyl iodide similarly gives (20; R = Et) and (22; R = Et) in the ratio 2 : 5.

When methyl or ethyl fluorosulphate was used as alkylating agent a faster reaction (24 h) ensued but more complex mixtures were produced. However the respective alkyl- and acyl-rhodium(III) porphyrin complexes were again produced. The fate of the rhodium atom displaced from the porphyrin ring has not been investigated. These reactions involve oxidative addition of the alkyl iodide to rhodium(I) to give a six-co-ordinate rhodium(III) species [(18) ⟶ (19); partial formulae]. The rhodium(III) species then undergoes competitive collapse into the centre of the porphyrin [(19) ⟶ (20)] or a 1,2-alkyl shift to the co-ordinated carbon monoxide giving the acyl-rhodium(III) complex (21), which then collapses into the central cavity of the porphyrin ring [(21) ⟶ (22)]. The dirhodium(I) complex of the *meso*-acetoxyporphyrin (6; X = C·OAc, $R^1 = R^3 = R^5 = Et$, $R^2 = R^4 = Me$) also reacted with methyl iodide, but gave a mixture of four products, two methyl- and two acetyl-rhodium(III) porphyrins. It has not proved possible to separate these, but spectral data (n.m.r., u.v., i.r., and mass) suggest that the four products are the expected methyl- and acetyl-rhodium(III) complexes (23; X = C·OAc, $R^1 = R^3 = R^5 = Et$, $R^2 = R^4 = Me$, $R^6 = Me$ or COMe) together with the

[17] E. Cetinkaya, A. W. Johnson, M. F. Lappert, G. M. McLaughlin, and K. W. Muir, *J.C.S. Dalton*, 1974, 1236.
[18] G. A. Taylor and M. Tsutsui, *J. Chem. Educ.*, 1975, **52**, 715.
[19] R. Grigg, R. J. Hamilton, M. L. Jozefowicz, C. H. Rochester, R. J. Terrell, and H. Wickwar, *J.C.S. Perkin II*, 1973, 407.

corresponding *meso*-unsubstituted rhodium(III) complexes (20; R = Me) and (22; R = Me). Loss of a *meso*-oxy-substituent has been observed previously.[13,20] Oxidative addition of methyl iodide to rhodium(I) carbonyl complexes bearing phosphine and related ligands is known to give methyl- or acetyl-rhodium(III) complexes or mixtures of both.[21-23]



The dirhodium(I) complex of the azaporphyrin (6; X = N, $R^1 = R^2 = R^4$ = Et, $R^3 = R^5$ = Me) reacts with methyl iodide to give a mixture of the methyl- and acetyl-rhodium(III) complexes (23; X = N, $R^1 = R^2 = R^4$ = Et, $R^3 = R^5$ = Me, R^6 = Me or COMe), together with a third product (a mixture of isomers), which still contains one rhodium-bound carbon monoxide ligand (ν 2 020 cm^{-1}). The dirhodium(I) precursor exhibits i.r. bands at 2 005 and 2 060 cm^{-1} and a similar pattern is shown by all the macrocycle complexes containing a dicarbonylrhodium unit. The n.m.r. spectrum of the unidentified product shows three or four signals, depending on the method of preparation, of nearly equal intensity between τ 13.00—13.70 for RhMe groups, all of which show Rh,H-coupling. However the position of the signals is significantly lower than that of the methyl-rhodium(III) azaporphyrin (23; X = N, $R^1 = R^2 = R^4$ = Et, $R^3 = R^5$ = Me, R^6 = Me), which occurs at τ 16.93 and this, together with the i.r. evidence of co-ordinated carbon monoxide, suggests that the rhodium has not collapsed into the centre of the azaporphyrin ring. Further work on this system is under way to explore the possibility that co-ordination of the *meso*-nitrogen atom to rhodium is stabilising a methyl-rhodium(III) intermediate.

The dirhodium(I) complexes also undergo oxidative addition reactions with carboxylic anhydrides. Typically the acyl-rhodium(III) complexes (22; R = Me, Et, or Pr^n) are formed in 82—92% yield by heating a solution of (4; R = Me) in chloroform with an excess of the appropriate anhydride. There is an induction period of up to 3 h for these reactions. Reaction in the neat anhydride at higher temperatures effects partial decarbonylation to give mixtures of the alkyl- and acyl-rhodium(III) porphyrins. Thus heating (4; R = Me) in boiling acetic anhydride gives a mixture of methyl- (20; R = Me) (21%) and acetyl- (22; R = Me) (67.5%) rhodium(III) porphyrins, and (4; R = Me) and benzoic anhydride at 110 °C for 3 h give a mixture of (20; R = Ph) (27%) and (22; R = Ph) (29%). The preparation of (20; R = Ph) by a different route has been reported,[3] but the *ortho*-phenyl proton signal was not located in the n.m.r. spectrum. We observe this signal as a doublet at τ 10.38. A small amount of methyl-rhodium(III) aetioporphyrin I together with the expected ethyl- and propionyl-rhodium(III) aetioporphyrins is formed when (4; R = Me) is heated in boiling propionic anhydride. The protons of the acyl substituents bound to rhodium give signals in the n.m.r. above τ 10 (Table).

N.m.r. signals (τ values; $CDCl_3$) of protons of *Rh*-acyl substituents of aetioporphyrin I complexes

Rh^{III} substituent	β-H	γ-H	δ-H
COMe	13.95		
COEt	14.24	12.26	
COPr-	14.23	11.90	11.60
COPh	8.50 †	4.55 ‡	4.03 §
O_2CMe *	10.78		
O_2CEt *	10.55	11.7	

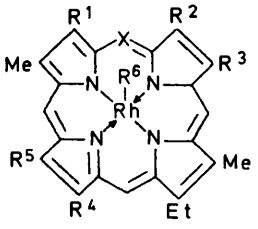
* Thiaporphyrin complexes (24; R = Me or Et). † *o*-H. ‡ *m*-H. § *p*-H.

Maximum shielding in the n.m.r. spectra of (22) occurs for the protons adjacent to the carbonyl group, *i.e.* the protons attached to the β-carbon atom.

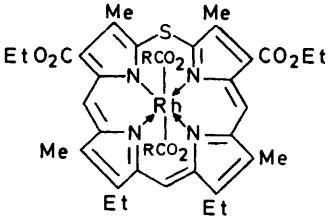
The azaporphyrin (6; X = N, $R^1 = R^2 = R^4$ = Et, $R^3 = R^5$ = Me) in hot acetic anhydride–benzene cleanly gives the corresponding acetyl-rhodium(III) complex (23; X = N, $R^1 = R^2 = R^4$ = Et, $R^3 = R^5$ = Me, R^6 = COMe) (67.6%), whereas the dirhodium(I) complex of the *meso*-acetoxyporphyrin (6; X = C·OAc, $R^1 = R^3 = R^5$ = Et, $R^2 = R^4$ = Me) again gave, under a variety of conditions, a mixture of two methyl- and two acetyl-rhodium(III) porphyrins similar to that obtained from the corresponding methyl iodide reaction. In contrast to the dirhodium(I) complexes of porphyrins and azaporphyrins, the thiaphlorin complex (10) reacts with acetic and propionic anhydrides to give the di-acyloxy-rhodium(III) complexes of the thiaporphyrin (24; R = Me or Et). The change in oxidation state of the macrocycle is evidenced by the n.m.r. spectra of (24; R = Me or Et) in which the *meso*-protons give signals at τ −1.32 (2 H) and −0.06 (1 H) [(24; R = Me)] or −1.29 (2 H) and −0.03 (1 H) [(24; R = Et)]. The signals for the protons of the acyloxy-groups bound to rhodium in (24) occur at significantly lower field than the corresponding signals for the acetyl- and propionyl-rhodium(III) porphyrins and azaporphyrin (Table), as

[20] H. H. Inhoffen, J. H. Fuhrhop, and F. von der Haar, *Annalen*, 1966, **700**, 92.
[21] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 597; G. Deganello, P. Ugualiati, B. Crociani, and U. Belluco, *ibid.*, 1969, 2726.
[22] D. Forster, *J. Amer. Chem. Soc.*, 1975, **97**, 951.
[23] H. D. Empsall, E. M. Hyde, C. E. Jones, and B. L. Shaw, *J.C.S. Dalton*, 1974, 1980.

would be expected since they are further removed from the influence of the ring current. The thiaphlorin complex (10) has a potential redox system rhodium(III)–thiaphlorin ⇌ rhodium(I)–thiaporphyrin which may affect the nature of the product.



(23)



(24)

Carboxylic anhydrides have been little used in oxidative addition reactions to date [24] but, in our system at least, they are preferable to acyl halides since the latter tend to give rise to the diprotonated porphyrin salt (15). However, aroyl halides are not so sensitive in this respect; benzoyl chloride and (4; R = Me) at 110 °C for 1 h give the benzoyl-rhodium(III) complex (22; R = Ph) (82%).

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. N.m.r. spectra were determined for solutions in $CDCl_3$ with a Bruker WP90 instrument, and mass spectra with an A.E.I. MS902 spectrometer operating at 70 eV. I.r. spectra were determined for KBr discs. T.l.c. separations were performed on Merck Kieselgel 60PF, and for column chromatography Woelm neutral alumina or silica gel was employed. Light petroleum refers to the fraction b.p. 40—60 °C. Chloroform used in the preparation of the dirhodium(I) complexes of porphyrins was purified by passage through a column of neutral alumina.

Cobalt(III) *Aetio-oxophlorin.*—This was prepared by adaptation of the method used for cobalt octaethyloxophlorin.[16] Cobalt(II) aetioporphyrin I (360 mg) gave dipyridinecobalt(III) aetio-oxophlorin (260 mg, 53.6%) as dark blue prisms (from pyridine–water), m.p. >300° (Found: C, 70.95; H, 6.4; N, 11.9. $C_{42}H_{45}CoN_6O$ requires C, 71.15; H, 6.4; N, 11.85%); for n.m.r. spectrum see Figure 3.

meso-*Acetoxyaetioporphyrin I.*—Acetic anhydride (4 ml) was added to aetio-oxophlorin I (100 mg) [15] in pyridine (10 ml) with stirring. After 0.5 h the mixture was diluted with water (100 ml) and acetic acid (35 ml) and extracted with methylene chloride. The organic layer was separated and washed with saturated sodium hydrogen carbonate solution and then with water. The dried (Na_2SO_4) organic layer was evaporated and the residue crystallised from methylene chloride–methanol to give the product [15] as purple prisms (107 mg, 99%), m.p. >300° (Found: C, 75.6; H, 7.45; N, 10.05. Calc. for $C_{34}H_{40}N_4O_2$: C, 76.1; H, 7.5; N, 10.45%), τ −0.06 (s, 2 × *meso*-H), 0.10 (s, *meso*-H), 5.97 (q, 4 × C*H*$_2$Me), 6.40, 6.41, 6.44, and 6.52 (all s, 4 × Me), 7.08 (s, OAc), and 8.16 (m, 4 × CH$_2$*Me*), $\nu_{max.}$ 1 775 cm^{-1}. Attempted purification by chromatography on alumina (Spence type H) caused hydrolysis to the oxophlorin.

Rhodium Complexes

μ-*Octaethylporphyrinato-bis*[*dicarbonylrhodium*(I)] (4; R = Et).—A solution of di-μ-chloro-bisdicarbonylrhodium (100 mg) in chloroform (5 ml) was added to a solution of octaethylporphyrin (100 mg) in chloroform (25 ml) containing anhydrous sodium carbonate or anhydrous sodium acetate (500 mg). After 0.5 h at room temperature the solution was poured into water and the chloroform layer washed with water (3 ×), dried (Na_2SO_4), and then concentrated to a small volume. Light petroleum was added to induce crystallisation. The product (129 mg, 98%) separated as green-blue needles, m.p. >300° (Found: C, 56.65; H, 5.05; N, 6.6. Calc. for $C_{40}H_{44}N_4O_4Rh_2$: C, 56.45; H, 5.2; N, 6.6%). The complex was identical with that described previously.[3]

μ-*Aetioporphyrinato-bis*[*dicarbonylrhodium*(I)] (4; R = Me).—Aetioporphyrin I (100 mg) in a similar manner gave the corresponding product (147 mg, 89%) as dark brown *needles* (from chloroform–light petroleum), m.p. >300° (Found: C, 54.45; H, 4.55; N, 7.2. $C_{36}H_{36}N_4O_4Rh_2$ requires C, 54.4; H, 4.55; N, 7.05%), τ −0.30 (s, 2 × *meso*-H), 0.00 (s, 2 × *meso*-H), 6.04 (m, 4 × C*H*$_2$Me), 6.44 (s, 2 × Me), 6.48 (s, 2 × Me), 8.18 (t, 2 × CH$_2$*Me*), and 8.42 (t, 2 × CH$_2$*Me*), $\nu_{max.}$ 1 990 and 2 055 cm^{-1}. A large-scale preparation from aetioporphyrin (1 g) with a reaction time of 2.5 h gave the product (1.4 g, 85%) in lower yield.

μ-*Deuteroporphyrinato-bis*[*dicarbonylrhodium*(I)].—Deuteroporphyrin (5a) (100 mg) was treated with di-μ-chloro-bisdicarbonylrhodium (100 mg) as above. The product (140 mg, 88%) crystallised from chloroform–light petroleum as brown *needles*, m.p. >300° (Found: C, 50.45; H, 3.65; N, 6.6. $C_{36}H_{30}N_4O_8Rh_2$ requires C, 50.7; H, 3.55; N, 6.55%), τ −0.40 to 0.04 (6 × s, *meso*-H of two isomers), 0.93 (d, β-H of two isomers), 1.10 (s, β-H), 5.66 (m, 2 × CH$_2$), 6.20—6.52 (m, 2 × CO$_2$*Me* and 4 × Me), and 6.68—7.06 (two overlapping t, 2 × CH$_2$), $\nu_{max.}$ 1 740, 2 000, and 2 050 cm^{-1}.

μ-(*Protoporphyrinato IX*)-*bis*[*dicarbonylrhodium*(I)].—Protoporphyrin IX (5b) (100 mg) was treated with di-μ-chloro-bisdicarbonylrhodium (100 mg) in chloroform for 10 min. The product crystallised from chloroform–light petroleum as brown *needles* (150 mg, 97%), m.p. >300° (Found: C, 53.3; H, 4.2; N, 6.4. $C_{40}H_{36}N_4O_8Rh_2$ requires C, 53.0; H, 4.0; N, 6.2%), τ −0.50 to 0.02 (m, *meso*-H signals of two isomers), 3.40—4.00 (m, allyl H), 5.65br (q, 2 × CH$_2$), 6.30—6.60 (m, 2 × CO$_2$Me and 4 × Me), and 6.70—7.07 (two overlapping t, 2 × CH$_2$), $\nu_{max.}$ 1 740, 1 995, and 2 050 cm^{-1}.

μ-(meso-*Acetoxyaetioporphyrinato*)-*bis*[*dicarbonylrhodium*(I)].—*meso*-Acetoxyaetioporphyrin (6; X = C·OAc, R^1 = R^3 = R^5 = Et, R^2 = R^4 = Me) (59 mg) and di-μ-chlorobis-dicarbonylrhodium (90 mg), were treated in the usual way; chromatography (alumina; benzene) gave the product (68 mg, 73%) as purple *needles* from chloroform–methanol, m.p. >300° (Found: C, 53.55; H, 4.5; N, 6.45. $C_{38}H_{38}N_4O_6Rh_2$ requires C, 53.55; H, 4.45; N, 6.55%), τ −0.27 (s, 2 × *meso*-H), 0.12 (s, *meso*-H), 5.98 (m, 4 × C*H*$_2$Me), 6.48—6.54 (4 × s, 4 × Me), 6.99 (s, OAc), 8.16 and 8.28 (2 × t, 2 × CH$_2$*Me*), and 8.43 (t, 2 × CH$_2$*Me*), $\nu_{max.}$ 1 770, 2 000, and 2 055 cm^{-1}.

Further elution of the column gave a red solution, which upon evaporation and crystallisation of the residue from chloroform gave a dirhodium oxophlorin complex (4.9 mg,

[24] D. M. Blake, S. Shields, and L. Wyman, *Inorg. Chem.*, 1974, **13**, 1595.

8.75%) identical with that obtained from aetio-oxophlorin (below).

μ-(3,7,13,17-Tetraethyl-2,8,12,18-tetramethyl-5-azaporphyrinato)-bis[dicarbonylrhodium(I)]. —3,7,13,17-Tetraethyl-2,8,12,18-tetramethyl-5-azaporphyrin (100 mg) was dissolved in hot chloroform (750 ml). Anhydrous potassium carbonate (2 g) was added to the cooled solution with stirring, followed by di-μ-chlorobisdicarbonylrhodium. After 2 min the solution was filtered through a silica gel column (10 × 15 cm). Removal of the solvent left the product as a purple solid (160 mg, 99%) which crystallised from benzene–methanol as purple-black needles, m.p. >300° (Found: C, 52.35; H, 4.5; N, 8.5. $C_{35}H_{35}N_5O_4Rh_2$ requires C, 52.85; H, 4.45; N, 8.8%).

Dicarbonyl-(8,12-diethyl-2,3,7,13,17,18-hexamethylcorrolato)rhodium(I) (9).—8,12-Diethyl-2,3,7,13,17,18-hexamethylcorrole (100 mg) was treated with di-μ-chlorobisdicarbonylrhodium (100 mg) in chloroform containing anhydrous sodium acetate for 10 min. After washing with water, the dried (Na_2SO_4), concentrated chloroform solution was chromatographed on silica gel. The first fraction (blue-red) contained the product (98 mg, 72%), m.p. 200—201°, which crystallised as purple *prisms* (extensive decomposition) from chloroform–light petroleum (Found: C, 62.5; H, 5.8; N, 9.4. $C_{31}H_{33}N_4O_2$ Rh requires C, 62.3; H, 5.7; N, 9.35%), τ 0.62, 0.82, and 0.86 (all s, 3 × *meso*-H), 6.20 (m, 2 × C*H*$_2$Me), 6.58, 6.66, 6.68, 6.76, 6.79, and 6.90 (all s, 6 × Me), 8.30 (t, CH$_2$*Me*), and 8.48 (t, CH$_2$*Me*), $\nu_{max.}$ 2 000 and 2 060 cm^{-1}.

(2,8-Bisethoxycarbonyl-13,17-diethyl-3,7,12,18-tetramethyl-5-thiaphlorinato)dicarbonylrhodium(I) (10).—2,8-Bisethoxycarbonyl-13,17-diethyl-3,7,12,18-tetramethyl-5-thiaphlorin (120 mg) in chloroform containing anhydrous sodium acetate (0.5 g) was treated with di-μ-chloro-bisdicarbonylrhodium (100 mg) for 15 min. The mixture was then washed with water, dried (Na_2SO_4), and evaporated. The residue was chromatographed (silica; $CHCl_3$) and the main green band gave the product (115 mg, 76%), m.p. >300°, which decomposed on attempted crystallisation from chloroform–light petroleum. A sample for analysis was obtained by further chromatography on alumina (Spence type H) (Found: C, 56.65; H, 5.2; N, 7.3; S, 4.15. $C_{35}H_{37}N_4O_6SRh$ requires C, 56.45; H, 4.95; N, 7.5; S, 4.3%), for n.m.r. data see Figure 1, $\nu_{max.}$ 1 697, 2 010, and 2 075 cm^{-1}.

Reaction of Aetio-oxophlorin with Di-μ-chloro-bisdicarbonylrhodium.—A solution of the rhodium complex (32 mg) in a little chloroform was added to a solution of aetio-oxophlorin (30 mg) in chloroform (10 ml) containing anhydrous sodium acetate. After 1.5 h the green solution was washed with water, dried (Na_2SO_4), and evaporated. The residue was chromatographed on alumina (Spence type H). Benzene eluted a red band which afforded the *dirhodium complex* (29 mg, 55.7%) formulated as (13; R = Me). Crystallisation from chloroform gave red needles (15 mg, 29%), m.p. >300° (Found: C, 53.5; H, 4.4; N, 6.9. $C_{36}H_{36}N_4O_5Rh_2$ requires C, 53.35; H, 4.45; N, 6.9%). The compound was paramagnetic and it was not possible to determine its n.m.r. spectrum. The i.r. spectrum showed $\nu_{max.}$ 1 593, 2 003, 2 015, and 2 065 cm^{-1}. Further elution with chloroform gave the *monorhodium complex* (15 mg, 35%), m.p. >300°, formulated as (12; R = Me), which decomposed on attempted crystallisation (Found: C, 59.45; H, 5.6; N, 8.05. $C_{34}H_{37}N_4O_3Rh,H_2O$ requires C, 59.45; H, 5.7; N, 8.15%), $\nu_{max.}$ 2 005 and 2 075 cm^{-1}.

Reaction of Octaethyloxophlorin with Di-μ-chloro-bisdicarbonylrhodium.—The rhodium complex (100 mg), dissolved in purified methylene chloride (5 ml) was added to a solution of octaethyloxophlorin (100 mg) in methylene chloride containing an excess of anhydrous sodium carbonate. After 2.5 h at room temperature the solution was washed with water (3 ×), dried (Na_2SO_4), and evaporated, and the residue chromatographed (silica; $CHCl_3$). The first fraction (brown-green) afforded a mixture (15 mg) of green and red products. The second fraction (red) gave, after evaporation and recrystallisation of the residue from chloroform–light petroleum, greenish needles of the *dirhodium complex* formulated as (13; R = Et) (29 mg, 18%), m.p. >300° (Found: C, 55.3; H, 4.85; N, 6.45. $C_{40}H_{44}N_4O_5Rh_2$ requires C, 55.45; H, 5.1; N, 6.45%), paramagnetic, $\nu_{max.}$ 1 588, 2 005, 2 015, and 2 065 cm^{-1}.

Oxidative Addition Reactions with Alkyl Halides and Fluorosulphates.—Methyl- and acetyl-rhodium(III) *aetioporphyrin* (I) [(20; R = Me) *and* (22; R = Me)]. (*A*) μ-Aetioporphyrinato-bis[dicarbonylrhodium(I)] (100 mg) was dissolved in chloroform (5 ml) and methyl iodide (1 ml) added. After 4 days at room temperature the solvent was removed and the residue separated by preparative t.l.c. (chloroform–benzene, 1 : 1). The first red band contained *methylrhodium*(III) *aetioporphyrin I* (20; R = Me) (19 mg, 25%), which crystallised from chloroform as red plates, m.p. >300° (Found: C, 66.6; H, 6.7; N, 9.2. $C_{33}H_{39}N_4Rh$ requires C, 66.65; H, 6.6; N, 9.4%), τ 0.06 (s, 4 × *meso*-H), 5.99 (q, 4 × C*H*$_2$Me), 6.44 (s, 4 × Me), 8.14 (t, 4 × CH$_2$*Me*), and 16.56 (d, $J_{Rh,H}$ 2.3 Hz, RhMe).

A second red band (lower R_F) afforded *acetylrhodium*(III) *aetioporphyrin I* (22; R = Me) (25 mg, 32%), which crystallised from chloroform–acetone as red plates, m.p. >300° (Found: C, 65.5; H, 6.4; N, 9.15. $C_{34}H_{39}N_4ORh$ requires C, 65.6; H, 6.3; N, 9.0%), τ 0.58 (s, 4 × *meso*-H), 6.26 (q, 4 × C*H*$_2$Me), 6.70 (s, 4 × Me), 8.30 (t, 4 × CH$_2$*Me*), and 13.95 (s, RhAc), $\nu_{max.}$ 1 720 cm^{-1}.

(*B*) A solution of μ-aetioporphyrinato-bis[dicarbonylrhodium(I)] (100 mg) in chloroform (3 ml) containing methyl fluorosulphate (10 drops) was kept in a refrigerator for 14 days. Preparative t.l.c. (chloroform–10% light petroleum) of the resulting complex mixture gave the methylrhodium(III) porphyrin (20; R = Me) (7 mg, 8%) and the acetylrhodium(III) porphyrin (22; R = Me) (18 mg, 22%), identical with those obtained in the methyl iodide reaction.

Reaction at room temperature gave an even more complex mixture.

Ethyl- and Propionyl-rhodium(III) *aetioporphyrin I* [(20; R = Et) *and* (22; R = Et)].—(*A*) μ-Aetioporphyrinato-bis[dicarbonylrhodium(I)] (100 mg) and ethyl iodide (3 ml) in chloroform (3 ml) reacted at room temperature for 8 days. Preparative t.l.c. (chloroform–benzene, 1 : 1) afforded the ethylrhodium(III) complex (20; R = Et) (8 mg, 12%), identical with that described previously [3] together with the *propionylrhodium*(III) *complex* (22; R = Et) (25 mg, 31%), which crystallised from chloroform–light petroleum as red plates, m.p. >300° (Found: C, 66.0; H, 6.3; N, 8.65. $C_{35}H_{41}N_4ORh$ requires C, 66.0; H, 6.5; N, 8.8%), τ 0.49 (s, 4 × *meso*-H), 6.24 (q, 4 × C*H*$_2$Me), 6.68 (s, 4 × Me), 8.28 (t, 4 × CH$_2$*Me*), 12.26 (t, RhCO·CH$_2$*Me*), and 14.24 (q, RhCOC*H*$_2$Me), $\nu_{max.}$ 1 715 cm^{-1}.

A similar reaction carried out in boiling solvent for 1.5 h gave an improved yield (47%) of the propionylrhodium(III) complex.

(*B*) When μ-aetioporphyrinato-bis[dicarbonylrhodium(I)] reacted with ethyl fluorosulphate at room temperature for 24 h a complex mixture of at least nine products was produced. Preparative t.l.c. with isolation of product from the first and third red bands gave small amounts of methyl- (from first band) and propionyl-rhodium(III) aetioporphyrins spectroscopically identical with those described above.

Methyl- and acetyl-rhodium(III) 3,7,13,17-*tetraethyl*-2,8,12,18-*tetramethyl*-5-*azaporphyrin*. A mixture of μ-(3,7,13,17-tetraethyl-2,8,12,18-tetramethyl-5-azaporphyrinato)-bis[dicarbonylrhodium(I)] (140 mg), chloroform (100 ml), anhydrous potassium carbonate (10 g), and methyl iodide (50 ml) was kept at room temperature for 2 days. The mixture was then filtered, the potassium carbonate washed with chloroform, and the filtrate evaporated to dryness under reduced pressure. The residue was chromatographed (Kiselgel G; benzene) and two red fractions were collected, each of which was rechromatographed (silica). The faster-running fraction contained *methylrhodium*(III) 3,7,13,17-*tetraethyl*-2,8,12,18-*tetramethyl*-5-*azaporphyrin* (31 mg, 29.5%), red rods (chloroform–methanol), m.p. 295° (decomp.) (Found: C, 64.25; H, 6.55; N, 11.95. $C_{32}H_{38}N_5Rh$ requires C, 64.5; H, 6.45; N, 11.75%), τ 0.57 (s, 2 × *meso*-H), 0.73 (s, *meso*-H), 5.80—6.52 (overlapping q, 4 × C*H*$_2$Me), 6.58 (s, 2 × Me), 6.69 (s, 2 × Me), 8.12 (t, 2 × CH$_2$*Me*), 8.34 (t, 2 × CH$_2$*Me*), and 16.93 (d, $J_{Rh,H}$ 3.2 Hz, RhMe).

A second fraction contained the uncharacterized methylrhodium compound (24 mg).

The slower moving fraction gave acetylrhodium(III) 3,7,13,17-tetraethyl-2,8,12,18-tetramethyl-5-azaporphyrin (28 mg, 25.5%), identical with that prepared from the rhodium(I) complex and acetic anhydride (below).

Oxidative Addition Reactions with Carboxylic Anhydrides.—*Acetylrhodium*(III) *aetioporphyrin I* (22; R = Me). (*A*) μ-Aetioporphyrinato-bis[dicarbonylrhodium(I)] (100 mg) was boiled under reflux in acetic anhydride (3 ml) and chloroform (5 ml) for 6 h (induction period 3 h). The product (22; R = Me) (64 mg, 82%) separated out after removal of chloroform under reduced pressure and was identical with that described previously.

(*B*) μ-Aetioporphyrinato-bis[dicarbonylrhodium(I)] (55 mg) was boiled under reflux in acetic anhydride (6 ml) for 1 h (induction period 30 min). Preparative t.l.c. (benzene–chloroform, 45 : 55) gave methylrhodium(III) aetioporphyrin I (8.6 mg, 21%) and acetylrhodium(III) aetioporphyrin I (29 mg, 67.5%).

Propionylrhodium(III) *aetioporphyrin I* (22; R = Et). (*A*) μ-Aetioporphyrinato-bis[dicarbonylrhodium(I)] (100 mg) was boiled under reflux in propionic anhydride (3 ml) and chloroform (5 ml) for 4 h (1.5 h induction period). The product (74 mg, 92%), isolated in the usual way, was identical with that described previously.

(*B*) μ-Aetioporphyrinato-bis[dicarbonylrhodium(I)] (90 mg) was suspended in propionic anhydride (5 ml) and boiled under reflux for 1 h. The mixture was then evaporated under reduced pressure and the residue dissolved in chloroform, washed with aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and separated by preparative t.l.c. The first red band afforded a 1 : 1 mixture (n.m.r.) (15 mg) of methyl- and ethyl-rhodium(III) aetioporphyrin(I). The second band gave propionylrhodium(III) aetioporphyrin I (63 mg, 78%).

Butyrylrhodium(III) *aetioporphyrin I* (22; R = Pr^n). μ-Aetioporphyrinato-bis[dicarbonylrhodium(I)] (100 mg) was boiled under reflux in a mixture of butyric anhydride (3 ml) and chloroform (5 ml) for 4.5 h (3 h induction period). The *product* (75 mg, 92%) was isolated in the usual way. Crystallisation from chloroform–acetone gave red needles, m.p. >300° (Found: C, 64.65; H, 6.5; N, 8.35. $C_{36}H_{43}N_4ORh,H_2O$ requires C, 64.65; H, 6.8; N, 8.35%), τ 0.35 (s, 4 × *meso*-H), 6.16 (q, 4 × C*H*$_2$Me), 6.60 (s, 4 × Me), 8.24 (t, 4 × CH$_2$*Me*), 11.60 (t, RhCO·CH$_2$·CH$_2$*Me*), 11.90 (m, RhCO·C*H*$_2$·CH$_2$Me), and 14.13 (t showing Rh,H coupling, RhCO·C*H*$_2$·CH$_2$Me), $\nu_{max.}$ 1 715 cm^{-1}.

Phenyl- and benzoyl-rhodium(III) *aetioporphyrin I* [(20; R = Ph) *and* (22; R = Ph)]. (*A*) μ-Aetioporphyrinato-bis[dicarbonylrhodium(I)] (100 mg) and benzoic anhydride (500 mg) were boiled under reflux in chloroform (5 ml) for 8 h. Preparative t.l.c. (benzene–chloroform, 1 : 1) gave *benzoylrhodium*(III) *aetioporphyrin I* (25 mg, 29%), m.p. >300°, which crystallised from chloroform–petroleum as purple needles (Found: C, 68.35; H, 6.0; N, 8.15. $C_{39}H_{41}N_4ORh$ requires C, 68.4; H, 6.85; N, 8.2%), τ 0.70 (s, 4 × *meso*-H), 4.03 (t showing *meta*-coupling, *p*-H of COPh), 4.55 (t, showing *meta*-coupling, 2 × *m*-H of COPh), 6.24 (q, 4 × C*H*$_2$Me), 6.68 (s, 4 × Me), 8.29 (t, 4 × CH$_2$*Me*), and 8.50 (d, showing *meta*-coupling, 2 × *o*-H of COPh), $\nu_{max.}$ 1 680 and 1 730 cm^{-1}.

(*B*) An improved yield (82%) of the benzoylrhodium(III) complex was obtained by heating μ-aetioporphyrinato-bis[dicarbonylrhodium(I)] in benzoyl chloride for 1 h at 110 °C, followed by preparative t.l.c. of the crude product.

(*C*) μ-Aetioporphyrinato-bis[dicarbonylrhodium(I)] (100 mg) and benzoic anhydride (200 mg) were mixed and heated at 110 °C for 3 h. Preparative t.l.c. (benzene–chloroform, 1 : 1) gave *phenylrhodium*(III) *aetioporphyrin I* (23 mg, 27%), m.p. >300°, red plates from chloroform–light petroleum (Found: C, 67.6; H, 6.2; N, 8.3. $C_{38}H_{41}N_4Rh,H_2O$ requires C, 67.65; H, 6.4; N, 8.3%), τ 0.00 (s, 4 × *meso*-H), 4.97 (t, *p*-H of RhPh), 5.54 (t, 2 × *m*-H of RhPh), 6.01 (q, 4 × C*H*$_2$Me), 6.46 (s, 4 × Me), 8.17 (t, 4 × CH$_2$*Me*), and 10.38 (d, 2 × *o*-H of RhPh).

A second red band from the t.l.c. plate afforded benzoylrhodium(III) aetioporphyrin (25 mg, 29%).

Acetylrhodium(III) 3,7,13,17-*Tetraethyl*-2,8,12,18-*tetramethyl*-5-*azaporphyrin*. μ-(3,7,13,17-Tetraethyl-2,8,12,18-tetramethyl-5-azaporphyrinato)-bis[dicarbonylrhodium(I)] (100 mg) was heated on a water-bath in acetic anhydride (150 ml) and benzene (25 ml) containing anhydrous potassium carbonate (10 g) for 24 h. The mixture was then cooled and poured into water (300 ml), the acetic acid was neutralised with sodium hydrogen carbonate, and the mixture was extracted with chloroform. The extract was washed with aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and filtered through a short column of alumina. The solvent was removed from the red filtrate to leave the *product* (53 mg, 67.6%), which crystallised from chloroform–methanol–pentane as red rods, slowly decomposing above 250 °C (Found: C, 62.75; H, 6.0; N, 10.65. $C_{33}H_{38}N_5ORh,0.5H_2O$ requires C, 62.65; H, 6.25; N, 11.05%), τ 0.50 (s, 2 × *meso*-H), 0.69 (s, *meso*-H), 6.00 (q, 2 × C*H*$_2$Me), 6.30 (q, 2 × C*H*$_2$Me), 6.58 (s, 2 × Me), 6.72 (s, 2 × Me), 8.14 (t, 2 × CH$_2$*Me*), 8.35 (t, 2 × CH$_2$*Me*), and 13.47 (s, RhAc); $\nu_{max.}$ 1 728 cm^{-1}.

Diacetoxyrhodium(III) 2,8-*bisethoxycarbonyl*-13,17-*diethyl*-3,7,12,18-*tetramethyl*-5-*thiaporphyrin* (24; R = Me). (2,8-Bisethoxycarbonyl-13,17-diethyl-3,7,12,18-tetramethyl-5-thiaphlorin)dicarbonylrhodium(I) (50 mg) was dissolved in freshly redistilled acetic anhydride (1.2 ml) and the green

solution kept for 2 days at room temperature during which the solution turned brownish-green and a solid was precipitated. After neutralisation (K_2CO_3) and extraction ($CHCl_3$) followed by removal of the solvent, the product was subjected to preparative t.l.c. (chloroform–methanol, 95 : 5) twice to give, after crystallisation from chloroform–light petroleum, brown *needles* (14 mg, 24.7%), m.p. >300° (Found: C, 55.45; H, 5.3; N, 6.5. $C_{37}H_{41}N_4O_8RhS$ requires C, 55.25; H, 5.1; N, 6.95%), τ −1.32 (s, 2 × *meso*-H), −0.06 (s, *meso*-H), 5.16 (q, 2 × OCH_2Me), 6.00 (s, 2 × Me), 6.12 (q, 2 × CH_2Me), 6.53 (s, 2 × Me), 8.20 (2 × overlapping t, 2 × OCH_2*Me* and 2 × CH_2*Me*), and 10.78 (s, 2 × OAc), $\nu_{max.}$ 1 630 (RhOAc) and 1 710 cm^{-1} (CO_2Et).

Dipropionyloxyrhodium(III) 2,8-*bisethoxycarbonyl*-13,17-*diethyl*-3,7,12,18-*tetramethyl*-5-*thiaporphyrin* (24; R = Et). This was prepared from (2,8-bisethoxycarbonyl-13,17-diethyl-3,7,12,18-tetramethyl-5-thiaphlorin)dicarbonylrhodium(I) (50 mg) and freshly distilled propionic anhydride (1.8 ml) in a manner analogous to that described above. The *product* (15 mg, 25.8%) crystallised from chloroform–light petroleum as brown needles, m.p. >300° (Found: C, 56.6; H, 5.75; N, 6.5; S, 4.1. $C_{39}H_{45}N_4O_8RhS$ requires C, 56.2; H, 5.4; N, 6.7; S, 3.8%), τ −1.29 (s, 2 × *meso*-H), −0.03 (s, *meso*-H), 5.16 (q, 2 × OCH_2Me), 6.03 (s, 2 × Me), 6.12 (q, 2 × CH_2Me), 6.55 (s, 2 × Me), 8.11—8.32 (m, 2 × OCH_2*Me* and 2 × CH_2Me), 10.55 (q, 2 × O·CO·CH_2Me), and 11.7 (t, 2 × O·CO·CH_2*Me*), $\nu_{max.}$ 1 625, 1 645 (RhO·COEt), and 1 710 cm^{-1} (CO_2Et).

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