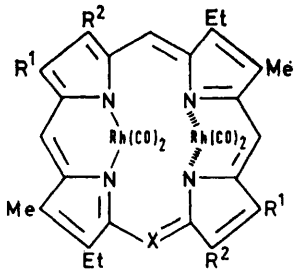
Dicarbonylrhodium(I) Complexes of Polypyrrole Macrocycles. Part 2.[1] Oxidative Addition Reactions with Aldehydes, Formates, β-Oxo-esters, Methyl Ketones, and Aryl Halides

By **Ajita M. Abeysekera, Ronald Grigg,* Jadwiga Trocha-Grimshaw,** and **Venkatappa Viswanatha,** Department of Chemistry, Queen's University, Belfast BT9 5AG, Northern Ireland

Out-of-plane bisdicarbonylrhodium complexes of etioporphyrin I and a monoazaporphyrin undergo oxidative addition reactions with a variety of substrates RX [R = aryl, acyl, arylcarbonyl, alkoxycarbonyl, ethoxycarbonylmethyl, $R'COCH_2$, or I; X = H or Br (usually) or I or CH_2COMe (in certain cases)]. One rhodium atom is detached from the macrocycle. The remaining $R-Rh^{III}$ species is captured by the central porphyrin cavity, retaining R, but with loss of X, to give $R-Rh^{III}$-etioporphyrin I or -monoazaporphyrin. Several new types of oxidative addition reaction have been observed, including insertion of rhodium into the $C_\alpha-H$ bond of a methyl ketone. The first isolation of stable acylrhodium(III) complexes from the reaction of rhodium(I) complexes with aldehydes is reported, and an improved method for preparing rhodium(III) porphyrins is described.

We have previously reported the preparation of out-of-plane rhodium(I) complexes of etioporphyrin I (1a) and



(1) a; X = CH, R^1 = Et, R^2 = Me
b; X = N, R^1 = Me, R^2 = Et

the monoazaporphyrin (1b).[1] These complexes were found to undergo oxidative addition reactions with alkyl halides and carboxylic anhydrides,[1] and we have briefly reported other examples of oxidative addition reactions.[2]

Oxidative addition reactions (Scheme 1) are a feature of the chemistry of low-valent transition metal complexes and are crucial to many catalytic processes. In these

$$M^{n+} + X-Y \longrightarrow X-M^{(n+2)+}-Y$$

Scheme 1

reactions the transition metal complex reacts with a reagent X–Y to form an adduct in which the stereochemistry of the metal ion has, of necessity, altered and the formal oxidation state of the metal has increased by two. Oxidative addition reactions are particularly important in the chemistry of d^8 (Rh^I, Ir^I, Os^0, Ru^0, *etc.*) and d^{10} (Pt^0, Ni^0, and Pd^0) metal complexes but the deceptive simplicity of Scheme 1 hides a complex mechanistic situation. Recently a number of oxidative ad-

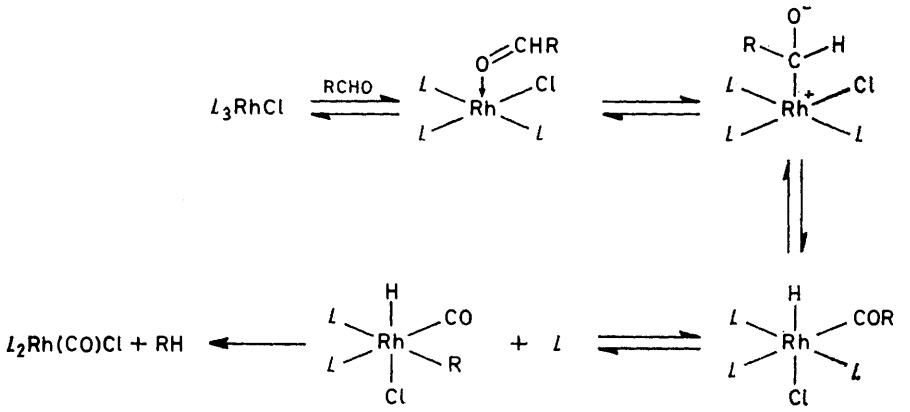
[1] Part 1, A. M. Abeysekera, R. Grigg, J. Trocha-Grimshaw, and V. Viswanatha, *J.C.S. Perkin I*, 1977, 36.

[2] A. M. Abeysekera, R. Grigg, J. Trocha-Grimshaw, and V. Viswanatha, *J.C.S. Chem. Comm.*, 1976, 227; *Tetrahedron Letters*, 1976, 3189.

dition reactions have been subjected to close scrutiny to distinguish amongst free radical,[3] ionic,[4] and concerted mechanisms.[5] In particular, it now seems that the oxidative addition reactions of alkyl halides to low valent transition metal complexes may involve competing radical and ionic (S_N2) processes. In such cases the mechanism will be sensitive to structural variations in both substrate and metal complex. Nevertheless, the uncertainty about mechanistic detail has not prevented the development of many catalytic processes involving oxidative addition as a key step, *e.g.* homogeneous catalytic hydrogenation,[6] catalytic decarbonylation of aldehydes,[7,8] catalytic conversion of methanol into acetic acid,[9] *etc.* With regard to the reactions discussed in this paper we have little information regarding the detailed mechanisms of the various oxidative additions apart from their sensitivity to reagent purity and our previous observation of an induction period in the oxidative addition of carboxylic anhydrides to the complexes (1a and b).[1]

Conventional rhodium(I) complexes undergo a wide range of oxidative addition reactions. However the rhodium(I) complexes (1a and b) seemed of special interest because (*a*) their unusual stereochemistry favours the generation of a reactive organorhodium(III) species close to a strongly co-ordinating tetradentate site (the central porphyrin cavity) and thus the porphyrin or monoazaporphyrin ring might prove capable of intercepting and stabilising a transient intermediate; (*b*) the reactivity of rhodium(I) species of the type $(N)_2Rh(CO)_2$ (N = donor nitrogen) in oxidative addition reactions had not hitherto been studied and compounds (1a and b) therefore offered the possibility of observing novel types of such reactions; * (*c*) appropriate oxidative addition reactions would be expected to produce a range of organorhodium(III) porphyrin derivatives of interest in connection with the influence of biochemical ligands on the transition metal–carbon bond.

The decarbonylation of aldehydes to hydrocarbons is a synthetically useful reaction catalysed by rhodium(I) complexes. When carried out with a stoicheiometric amount of rhodium(I) complex the intramolecular reaction is highly stereoselective for retention of configuration.[8] The generally accepted mechanism for the reaction involves oxidative addition of the aldehyde C(1)–H bond to the rhodium(I) complex (Scheme 2). The acylrhodium(III) complexes have not been isolated or detected in these reactions but analogous complexes have been isolated from the reactions of rhodium(I) complexes with acyl halides.[10] Stable diacyl complexes $[(Ph_3P)_2Pt(COR)_2]$ were reported [11] to be formed when aldehydes (RCHO) reacted with the tetraphosphine-platinum complex $[(Ph_3P)_4Pt]$, but these were subsequently shown [12] to be the dicarboxylate complexes $[(Ph_3P)_2Pt(O_2CR)_2]$.



SCHEME 2

We find that both compounds (1a) and (1b) react with aldehydes with formation of stable acylrhodium(III) derivatives. Thus (1a) reacts with benzaldehyde at 110 °C (20 h) to give a mixture of the benzoylrhodium(III)

* This, of course, would be invalidated if the active species is a ligand exchange product $(N)_2Rh(CO)_2 + 2L \rightleftharpoons L(N)RhCO_2 \rightleftharpoons L_2Rh(CO)_2$.

[3] J. A. Labinger, A. V. Kramer, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1973, **95**, 7908; J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *ibid.*, 1972, **94**, 4043; A. V. Kramer and J. A. Osborn, *ibid.*, 1974, **96**, 7832.

[4] D. Forster, *J. Amer. Chem. Soc.*, 1975, **97**, 951; 1976, **98**, 846; K. S. Y. Lau, R. W. Fries, and J. K. Stille, *ibid.*, 1974, **96**, 4983; P. K. Wong, K. S. Y. Lau, and J. K. Stille, *ibid.*, p. 5956.

[5] R. G. Pearson, *Accounts Chem. Res.*, 1971, **4**, 152.

[6] B. R. James, 'Homogeneous Hydrogenation,' Wiley, New York, 1973.

[7] M. C. Baird, C. J. Nyman, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 348; R. F. Heck, 'Organotransition Metal Chemistry,' Academic Press, New York, 1974, p. 265.

[8] H. M. Walborsky and L. E. Allen, *J. Amer. Chem. Soc.*, 1971, **93**, 5465; J. Tsuji and K. Ohno, *Synthesis*, 1969, 157.

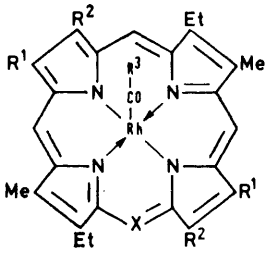
[9] F. E. Paulik and J. F. Roth, *Chem. Comm.*, 1968, 1578; J. F. Roth, J. H. Craddock, A. Hershman, and F. E. Paulik, *Chem. Technol.*, 1971, 600.

[10] M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 1347; K. Ohno and J. Tsuji, *J. Amer. Chem. Soc.*, 1968, **90**, 99; J. K. Stille, M. T. Regan, R. W. Fries, F. Huang, and T. McCarley, 'Homogeneous Catalysis-II,' A.C.S. Adv. in Chem. Series, No. 132, 1974.

[11] I. Harvie and R. D. W. Kemmitt, *Chem. Comm.*, 1970, 198.

[12] P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *J. Amer. Chem. Soc.*, 1970, **92**, 5873.

porphyrin (2a; R^3 = Ph) (43.5%) and the phenylrhodium(III) derivative (3a; R^3 = Ph) (7.5%). The monoazaporphyrin complex (1b) reacts similarly with benzaldehyde (C_6H_6; 80 °C; 3 days) to give a mixture of (2b; R^3 = Ph) (18%) and (3b; R^3 = Ph) (54%). The



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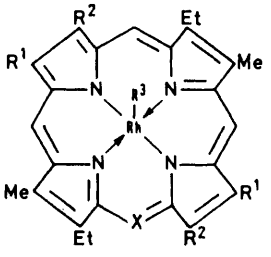
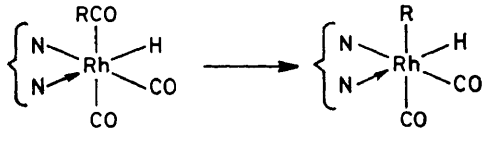


(3)

a; X = CH, R^1 = Et, R^2 = Me
b; X = N, R^1 = Me, R^2 = Et

mixtures were cleanly separated by preparative t.l.c.; the products from (1a) were identical with those prepared previously from (1a) and benzoic anhydride.[1] Valeraldehyde reacts (110 °C; 5 h) with (1a) to give the acylrhodium(III) complex (2a; R^3 = Bu^n) (33.5%), but in this case only a trace of (3b; R^3 = Bu^n) was detected. The mass spectrum of the valerylrhodium(III) complex (2a; R^3 = Bu^n) showed a strong peak at *m/e* 580 ($M - C_5H_8O$), due to loss of the valeryl substituent with hydrogen transfer to the rhodium porphyrin. The fate of the second dicarbonylrhodium moiety was not investigated in this or any of the other oxidative addition reactions described in this paper, and the possibility that it may assist at least some of the oxidative addition processes cannot be discounted.

In the absence of side reactions the ratio of (2) to (3) would be dependent upon the relative rates of collapse of the intermediate acylrhodium(III) hydride (4) into the central porphyrin cavity and the rate of migration of R to Rh to give the aryl- (or alkyl-)rhodium complex



(4) (5)

(5).* However, the sensitivity of the ratio of (3) to (2) to reaction conditions is illustrated by results from the reaction of (1a) with both purified and impure benzaldehyde under nitrogen in the presence of air. This reaction was carried out a total of six times and the yields were difficult to reproduce. Reactions in the presence of air were always faster (20 min to 2 h) than those carried out under nitrogen (6—20 h). The ratio of (3a; R^3 = Ph) to (2a; R^3 = Ph) varied between the extremes of 5 : 1 (impure benzaldehyde; air) to 1 : 6 (purified benzaldehyde; nitrogen).

The complexes (1a and b) also react with formate esters by insertion into the C(1)–H bond in a reaction analogous (at least formally) to the aldehyde insertion. Thus (1a) reacts with both n-butyl and benzyl formates at 110 °C to give the corresponding alkoxycarbonylrhodium(III) porphyrins (6a; R^3 = Bu^n or $PhCH_2$) in *ca.* 40% yield. The monoazaporphyrin complex (1b) reacts with formates in an analogous way. Thus (1b) reacted in boiling n-propyl formate to give (6b; R^3 = Pr^n) and a small amount of (3b; R^3 = Pr^n). The n.m.r. signals for the propyl group attached to rhodium are virtually identical with those for the related propylrhodium(III) octaethylporphyrin.[13] We have also discovered another novel route to the alkoxycarbonylrhodium(III) porphyrin complexes. The complex (1a) reacts with ethyl and benzyl acetoacetates at 110 °C to give the corresponding alkoxycarbonyl derivatives (6a; R^3 = Et or $PhCH_2$).

TABLE 1

Carbonyl stretching frequencies (KBr discs) of acyl- and alkoxycarbonyl-rhodium(III) porphyrins and monoazaporphyrins

Compound	$\nu_{max.}$/cm^{-1}
(2a; R^3 = Ph)	1 685, 1 727
(2b; R^3 = Ph)	1 686, 1 727
(2a; R^3 = *p*-FC_6H_4)	1 690
(2a; R^3 = Bu^n)	1 715
(6a; R^3 = Et)	1 690
(6a; R^3 = Bu^n)	1 684 (1 630w, br)
(6a; R^3 = $PhCH_2$)	1 685 (1 640w, br)
(6b; R^3 = Pr^n)	1 688 (1 630w, br)

The preparation of alkoxycarbonylmetal derivatives is usually achieved by oxidative addition of the C–Cl bond of chloroformate esters to metal complexes [14] or by alkoxide ion attack on cationic metal carbonyl complexes.[15] One report of the preparation of an alkoxycarbonylrhodium(III) porphyrin has appeared involving nucleophilic attack of ethoxide on carbonylrhodium(III) *meso*-tetraphenylporphyrin chloride.[16] Apart from our own examples there is only one report [11] of the oxidative addition of the C(1)–H bond of a formate ester to a transition metal complex [$(Ph_3P)_4Pt$], to give the diester (7). The reaction of (1a) with β-oxo-esters involves carbon–carbon bond cleavage and, although novel, appears to be related to the recently reported decarbonylation of aliphatic β-diketones to monoketones (*e.g.* acetylacetone to ethyl methyl ketone) by chlorotristriphenylphosphinerhodium.[17]

* Although we have chosen to represent (4), (5), and Scheme 2 in terms of covalent structures, free radical or ionic intermediates may be involved. Ref. 8 proposes a radical pair with a pentacoordinate rhodium for the intermediate analogous to (5) in the decarbonylation of aldehydes by chlorotristriphenylphosphinerhodium.

[13] H. Ogoshi, J.-I. Setsune, T. Omura, and Z.-I. Yoshida, *J. Amer. Chem. Soc.*, 1975, **97**, 6461.

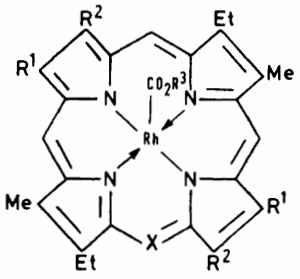
[14] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 443; G. Deganello, P. Uguagliati, B. Crociani, and U. Belluco, *J. Chem. Soc.* (*A*), 1969, 2726.

[15] L. Malatesta, G. Caglio, and M. Angoletta, *J. Chem. Soc.*, 1965, 6974.

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

[17] K. Kaneda, H. Azuma, M. Wayaku, and S. Teranioli, *Chem. Letters*, 1974, 215.

The carbonyl stretching frequencies of the various acyl- (2a and b) and alkoxycarbonyl- (6a and b) rhodium(III) derivatives are collected in Table 1. The doublet carbonyl signal for the benzoyl derivatives (2a and b; R^3 = Ph) is not due to crystal lattice effects, since the small amounts of two other products were isolated, neither of which contained a ring-opened cyclopropyl moiety. The more abundant of the minor products proved to be the acetylrhodium(III) complex (2b; R^3 = Me) which we had previously prepared by oxidative addition of methyl iodide or acetic anhydride to (1b).[1] This was contaminated with a trace of a product containing a cyclopropyl moiety which, from the chemical shift of the cyclopropyl protons (τ 12.0, 12.5, and 14.8; ratio 2 : 2 : 1) and its mass spectrum, was identified as the cyclopropylcarbonylrhodium(III) complex (2b; R^3 = cyclopropyl). The other product, which had a greater R_F value, was present in amounts insufficient for complete characterisation, but Fourier transform n.m.r. indicated that it was the methylrhodium(III) complex (3b; R^3 = Me), since it exhibited a doublet ($J_{Rh,H}$ 3.2 Hz) at τ 16.4.



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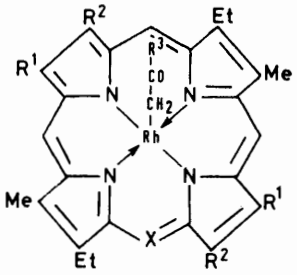
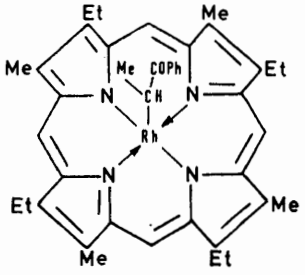


(8)

$(Ph_3P)_2\ Pt(CO_2Et)_2$

(7)

a; X = CH, R^1 = Et, R^2 = Me
b; X = N, R^1 = Me, R^2 = Et



(9)

doublet is retained in the solution spectra. It may reflect a conformational process involving two orientations of the phenyl ring with respect to the plane of carbonyl group and the plane of the macrocycle.* The i.r. spectrum (KBr disc) of the related acetylcobalt(III) etioporphyrin I [18] shows a carbonyl band at 1 722 cm^{-1}, whereas the ethoxycarbonylrhodium(III) *meso*-tetraphenylporphyrin [16] has a carbonyl band (KBr disc) at 1 700 cm^{-1}.

The n.m.r. spectra of the alkoxycarbonyl complexes (6a and b) show the expected variation of chemical shift of the protons of the ester moiety with increasing distance from the metal atom and porphyrin ring current (Table 2).

A third example of oxidative addition of C–H to the complexes (1a and b) is provided by their reactions with methyl ketones. Thus (1a) reacts with ketones MeCOR (R = Ph, cyclopropyl, or furyl) at 110—120 °C to give the rhodium(III) porphyrin derivatives (8a; R^3 = Ph, cyclopropyl, or furyl). A remarkable range of products was obtained from the reaction of the monoazaporphyrin complex (1b) with cyclopropyl methyl ketone. The major product (8b; R^3 = cyclopropyl) was analogous to that obtained from the porphyrin, but in this case

TABLE 2

^{1}H N.m.r. signals (τ values; $CDCl_3$) of alkoxycarbonylrhodium(III) etioporphyrin I and monoazaporphyrin complexes

$RhCO_2-\overset{\alpha}{C}-\overset{\beta}{C}-\overset{\gamma}{C}-\overset{\delta}{C}$

Compound	H_α	H_β	H_γ	H_δ
(6a; R^3 = Et)	9.38 (q)	11.37 (t)		
(6b; R^3 = Pr^n)	9.11 (br, t)			
(6a; R^3 = Bu^n)	9.55 (t)		10.96m	9.86 (t)
(6a; R^3 = $PhCH_2$)	8.56 (s)	5.18 (d) †		3.27 (m) ‡

† *ortho*-Protons of Ph. ‡ *meta*- and *para*-Protons of Ph.

* An *X*-ray crystal structure determination of (2a; R^3 = Ph) is in progress.

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

The reaction is not restricted to methyl ketones: (1a) and ethyl phenyl ketone react to give (9).* No reaction occurred when rhodium(III) etioporphyrin I acetate was heated with cyclopropyl methyl ketone, thus ruling out, under these conditions, nucleophilic attack of the ketone enolate on the rhodium(III) porphyrin as a source of (8a and b) and (9).

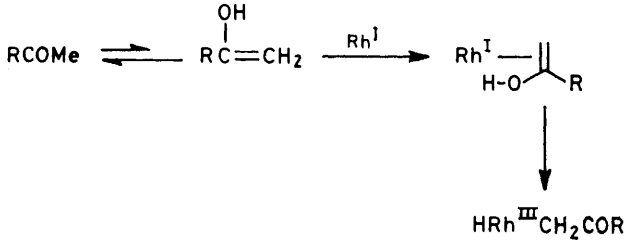
This insertion of rhodium into the C_α–H bond of a methyl ketone is a new type of oxidative addition reaction, although insertion into the doubly activated C–H bond of the central methylene group in β-diketones is well known.[19] Several mechanisms appear possible for this process. The reaction may be of the free radical type, involving abstraction of the α-hydrogen atom of the ketone followed by attack of the enolate radical on rhodium(I) (Scheme 3). Alternatively the enol form of the ketone may be the reactive species, forming an intermediate π-bonded rhodium(I) system which is then converted into a rhodium(III) hydride species; this then collapses into the porphyrin cavity (Scheme 4). These suggestions are not mutually exclusive since a π-complexed enolate radical is a possibility. The intervention of a cobalt(III) π-complexed enol has been suggested[20] for the biochemical conversion of vicinal diols into aldehydes mediated by coenzyme vitamin B_{12}, but other workers[21,22] favour a free-radical mechanism for this process.

$$X^{\bullet} + H{-}CH_2COR \longrightarrow XH + \dot{C}H_2COR$$

$$Rh^{I} + \dot{C}H_2COR \longrightarrow Rh^{II}CH_2COR$$

$$Rh^{II}CH_2COR + H{-}CH_2COR \longrightarrow HRh^{III}CH_2COR + \dot{C}H_2COR$$

SCHEME 3



SCHEME 4

When the complex (1a) was heated (110 °C) in cyclopropyl *p*-fluorophenyl ketone, the cyclopropyl ring underwent fission giving the organorhodium(III) porphyrin (10; R^1 = Me, R^2 = *p*-FC_6H_4) in 32% yield. In this case enolisation is a much higher energy process than for the methyl ketones, since it results in sp^2 hybridisation of a cyclopropyl carbon atom with consequent increase in angle strain in the cyclopropyl ring. Radical abstraction from the tertiary cyclopropyl carbon suffers a similar disadvantage. Thus reactions other than C–H bond insertion are favoured. Neutral rhodium(I) carbonyl complexes have long been known to undergo oxidative addition reactions with cyclopropanes, usually with incorporation of a carbon monoxide moiety,[23,24] *e.g.* cyclopropane and the dinuclear complex $[Rh_2(CO)_4Cl_2]$ give the rhodacyclopentanone (11).[23] Cyclopropanes bearing electron-withdrawing groups are less reactive to electrophilic species but are cleaved by nucleophiles. To date only one report,[25] without experimental detail, describing insertion of a neutral rhodium(I) species into an electronegatively substituted cyclopropane has appeared; this example contained a particularly strained cyclopropane moiety. More recently, the nucleophilic anionic rhodium(I) porphyrin complex (12) has been found to cause ring opening of cyclopropanes.[26] Indeed, in contrast to our product (8a; R = cyclopropyl) from (1a) and cyclopropyl methyl ketone, the anionic rhodium(I) porphyrin (12) and cyclopropyl methyl ketone give (10; R^1 = Et, R^2 = Me), illustrating the much greater nucleophilicity of (12) than of the neutral complexes (1a and b). The cleavage of the cyclopropyl ring of cyclopropyl *p*-fluorophenyl ketone by (1a) may be assisted by co-ordination of the 'displaced' bisdicarbonylrhodium moiety to the carbonyl oxygen atom [*e.g.* (13)] of the ketone, so aiding attack by the weakly nucleophilic dicarbonylrhodium(I) species.

We have previously reported the oxidative addition of alkyl halides to (1a and b),[1] and find that (1a and b) also react with aryl halides (110—130 °C). Thus (1a) reacted with bromo-, iodo-, and 1-bromo-4-fluoro-benzene to give approximately equal amounts of the aryl- (3a; R^3 = Ph or *p*-FC_6H_4) and arylcarbonyl- (2a; R^3 = Ph or *p*-FC_6H_4) rhodium(III) porphyrins. In contrast 1-bromo-4-cyanobenzene gave only the aryl complex

* Dialkyl ketones also react with (1a), and these reactions, together with those of β-diketones, which react in a manner different from β-oxo-esters, will form the basis of a subsequent paper.

[19] D. Gibson, *Co-ord. Chem. Rev.*, 1969, **4**, 225; S. Baba, T. Ogura, and S. Kawaguchi, *Bull. Soc. Chem. Japan*, 1974, **47**, 665.

[20] R. B. Silverman and D. Dolphin, *J. Amer. Chem. Soc.*, 1974, **96**, 7094; R. B. Silverman, D. Dolphin, T. J. Carty, E. K. Krodel, and R. H. Abeles, *ibid.*, p. 7096.

[21] B. T. Golding and L. Radon, *J.C.S. Chem. Comm.*, 1973, 939.

[22] C. Walling and R. A. Johnson, *J. Amer. Chem. Soc.*, 1975, **97**, 2405.

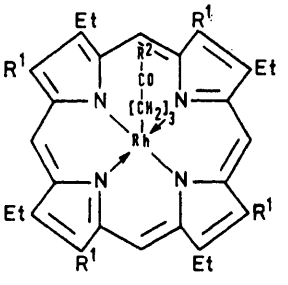
[23] D. M. Roundhill, D. N. Lawson, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 845.

[24] F. J. McQuillin and K. G. Powell, *J.C.S. Dalton*, 1972, 2129; L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, 1970, **92**, 3515; P. G. Gassman and J. H. Nikova, *J. Organometallic Chem.*, 1975, **92**, 81; J. Blum, C. Zlotogorski, and A. Zoran, *Tetrahedron Letters*, 1975, 1117.

[25] B. F. G. Johnson, J. Lewis, and S. W. Tam, *Tetrahedron Letters*, 1974, 3793.

[26] H. Ogoshi, J.-I. Setsune, and Z.-I. Yoshida, *J.C.S. Chem. Comm.*, 1975, 572.

[3a; $R^3 = p$-$(CN)C_6H_4$] (9.5%). The mass spectrum of (2a; $R^3 = p$-FC_6H_4), besides showing strong peaks at *m/e* 702 (M^+) and 579 ($M - FC_6H_4CO$), also had a strong peak at *m/e* 674 ($M - CO$). The azaporphyrin complex



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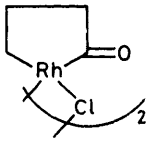
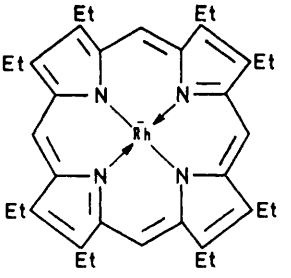
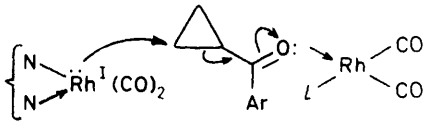


(11)

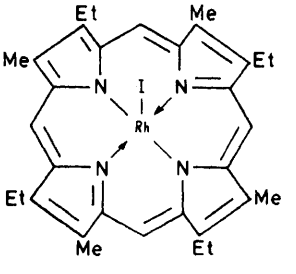


(12)

(1b) reacts with bromobenzene to give the phenylrhodium(III) azaporphyrin (3b; $R^3 = Ph$) (43%), and only a trace of the corresponding benzoylrhodium (III) derivative. Studies of equilibria between alkyl- and acylrhodium phosphine complexes show that the RCO*M* $\rightleftharpoons$



(13)



(14)

R*M*(CO) equilibrium constants decrease in the order (R =) aryl > methyl > n-alkyl.[27] Our systems are, of course, not at equilibrium, and the results with benzaldehyde and (1a) suggest that a complex situation exists.

[27] D. Egglestone and M. C. Baird, *J. Organometallic Chem.*, 1976, **113**, C25.

The complex (1a) also reacts with ethyl bromoacetate at 110 °C to give the ethoxycarbonylmethylrhodium(III) etioporphyrin (8a; $R^3 = OEt$). Care must be taken to purify the ethyl bromoacetate, because traces of acid cause decomposition of (1a). Iodine also reacts with (1a) in chloroform solution at room temperature to give rhodium(III) etioporphyrin iodide (14) (71%). The iodine reaction provides a simple ' one-pot ' synthesis of rhodium(III) porphyrins which is superior to the previously described method.[28] Thus the μ-porphyrinato-bis[dicarbonylrhodium(I)] complexes can be prepared *in situ* and immediately treated with iodine without prior isolation.

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. μ-Etioporphyrinato-bis[dicarbonylrhodium(I)] (1a) and μ-3,7,13,17-tetraethyl-2,8,12,18-tetramethyl-5-azaporphyrinato-bis[dicarbonylrhodium(I)] (1b) were prepared as described previously.[1]

Benzoyl- and Phenyl-rhodium(III) *Etioporphyrin I* (2a; $R^3 = Ph$) *and* (3a; $R^3 = Ph$).—(a) μ-Etioporphyrinato-bis[dicarbonylrhodium(I)] (80 mg) was heated at 110 °C, under nitrogen, with freshly distilled benzaldehyde (3 ml) for 20 h. The excess of benzaldehyde was removed under reduced pressure and the residue separated by preparative t.l.c. ($CHCl_3$). The faster moving red band afforded, after work-up in the usual way, phenylrhodium(III) etioporphyrin I (5 mg, 7.5%). The slower moving red band contained the benzoylrhodium(III) etioporphyrin I (30 mg, 43.5%). These products were identical (i.r., n.m.r., and mass spectra) with those reported from the reaction of μ-etioporphyrinato-bis[dicarbonylrhodium(I)] with benzoic anhydride.[1]

The reaction was repeated a further five times both with and without a nitrogen atmosphere, and using both pure and impure benzaldehyde. Reaction times varied from 20 min to 20 h and the ratio of phenyl- to benzoyl-rhodium(III) etioporphyrin I varied from 5 : 1 to 1 : 6. Reactions in air were significantly faster than those carried out under nitrogen.

(*b*) μ-Etioporphyrinato-bis[dicarbonylrhodium(I)] (100 mg) was heated at 110 °C in iodobenzene (2 ml) for 4 h. The products, isolated by preparative t.l.c., consisted of benzoylrhodium(III) etioporphyrin I (20 mg; 25%) and rhodium(III) etioporphyrin I iodide (23 mg, 26%).

(*c*) μ-Etioporphyrinato-bis[dicarbonylrhodium(I)] (100 mg) in bromobenzene (2 ml) at 110 °C for 5 h gave a mixture of phenyl- (15 mg, 18%) and benzoyl-rhodium(III) etioporphyrin I (12 mg, 14%).

p-*Fluorophenyl- and* p-*Fluorobenzoyl-rhodium*(III) *Etioporphyrin I* (3a; $R^3 = p$-FC_6H_4) *and* (2a; $R^3 = p$-FC_6H_4).—These were prepared (110 °C; 2 h) as above from 1-bromo-4-fluorobenzene (2 ml) and μ-etioporphyrinato-bis[dicarbonylrhodium(I)] (50 mg). The usual work-up afforded

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

(i) p-*fluorophenylrhodium*(III) *etioporphyrin I* (13 mg, 15%), m.p. >300°, red plates from chloroform–methanol (Found: C, 66.45; H, 6.0; N, 8.2; F, 2.8. $C_{38}H_{40}FN_4Rh$ requires C, 66.75; H, 6.0; N, 8.2; F, 2.8%), *m/e* 674 (M^+) and 579 ($M - C_6H_4F$), τ 0.20 (4 H, s, *meso*-H), 5.86 (2 H, t, *meta* ArH), 6.15 (8 H, q, CH_2Me), 6.58 (12 H, s, Me), 8.28 (12 H, t, CH_2Me), and 10.76 (2 H, t, *ortho* ArH); and (ii) p-*fluorobenzoylrhodium*(III) *etioporphyrin I* (12 mg, 13%), m.p. >300, red plates from chloroform–methanol (Found: C, 64.8; H, 5.6; N, 7.2; F, 2.75. $C_{39}H_{40}FN_4ORh,H_2O$ requires C, 65.0; H, 5.85; N, 7.7; F, 2.65%); τ 0.69 (4 H, *meso*-H), 4.93 (2 H, t, *meta* ArH), 6.31 (8 H, q, CH_2Me), 6.76 (12 H, Me), 8.37 (12 H, CH_2Me), and 8.56 (2 H, t, *ortho* ArH).

p-*Cyanophenylrhodium*(III) *Etioporphyrin I* [3a; R^3 = *p*-$(CN)C_6H_4$].—This was prepared (130 °C; 1 h) from μ-etioporphyrinato-bis[dicarbonylrhodium(I)] (50 mg) and 1-bromo-4-cyanobenzene (300 mg). Work-up in the usual way afforded the *product* (8 mg; 9.5%), m.p. >300°, as red needles from chloroform–methanol (Found: C, 68.25; H, 5.95; N, 10.15. $C_{39}H_{40}N_5Rh$ requires C, 68.7; H, 5.9; N, 10.25%); *m/e* 681 (M^+); τ 0.05 (4 H, s, *meso*-H), 5.42 (2 H, d, *meta* ArH), 6.06 (8 H, q, CH_2Me), 6.51 (12 H, s, Me), 8.24 (12 H, t, CH_2Me), and 10.51 (2 H, d, *ortho* ArH).

Valerylrhodium(III) *Etioporphyrin I* (2a; R^3 = Bu^n).—μ-Etioporphyrinato-bis[dicarbonylrhodium(I)] (80 mg) and freshly distilled valeraldehyde (3 ml) were heated at 110 °C for 5 h. Removal of the excess of aldehyde and preparative t.l.c. ($CHCl_3$) gave the *product* (20 mg, 33.4%) as red plates from chloroform–light petroleum, m.p. >300° (Found: C, 66.65; H, 6.85; N, 8.45. $C_{37}H_{45}N_4ORh$ requires C, 66.85; H, 6.8; N, 8.45%), *m/e* 664 (M^+), 580 ($M - C_5H_8O$), and 579 ($M - C_5H_9O$).

Benzoyl- and Phenyl-rhodium(III) 3,7,13,17-*Tetraethyl*-2,8,12,18-*tetramethyl*-5-*azaporphyrin* (2b; R^3 = Ph) *and* (3b; R^3 = Ph).—(a) μ-3,7,13,17-Tetraethyl-2,8,12,18-tetramethyl-5-azaporphyrinato-bis[dicarbonylrhodium(I)] (180 mg) was boiled under reflux for 3 days in a solution of benzaldehyde (30 ml) in benzene (100 ml) containing anhydrous potassium carbonate (2 g) while a nitrogen atmosphere was maintained. The cooled mixture was then filtered through a short column (silica) and washed through with benzene. The filtrate was evaporated under reduced pressure and the viscous residue separated by combined column (Kieselgel 60PF; benzene) and preparative t.l.c. into (i) the *phenylrhodium*(III) *azaporphyrin* (81 mg, 54%), red rods from chloroform–methanol, m.p. >300° (Found: C, 67.4; H, 6.1; N, 10.55. $C_{37}H_{40}N_5Rh$ requires C, 67.55; H, 6.15; N, 10.65%), *m/e* 657 (M^+); τ 0.12 (1 H, s, *meso*-H), 0.16 (2 H, s, *meso*-H) 4.93 (1 H, t, *para* ArH), 5.42 (2 H, t, *meta* ArH), 6.02 (8 H, m, CH_2Me), 6.52 (6 H, s, Me), 6.57 (6 H, s, Me), 8.18 (12 H, m, CH_2Me), and 10.15 (2 H, d, *ortho* ArH); and (ii) the *benzoylrhodium*(III) *azaporphyrin* (28 mg, 18%), red rods from chloroform–methanol, m.p. 263—266° (Found: C, 65.5; H, 5.75; N, 9.95. $C_{38}H_{40}N_5ORh,0.5H_2O$ requires C, 65.7; H, 5.95; N, 10.1%), *m/e* 685 (M^+) and 580 ($M - C_6H_5CO$); τ 1.1 (2 H, s, *meso*-H), 1.41 (1 H, s, *meso*-H), 4.10 (1 H, t showing slight *meta*-coupling, *para* ArH), 4.64 (2 H, t, *meta* ArH), 6.05 (4 H, m, CH_2Me), 6.30 (4 H, q, CH_2Me), 6.73 (6 H, s, Me), 6.95 (6 H, s, Me), 8.20 (6 H, t, CH_2Me), and 8.54 (8 H, m, CH_2Me and *ortho* ArH).

(b) μ-3,7,13,17-Tetraethyl-2,8,12,18-tetramethyl-5-azaporphyrinato-bis[dicarbonylrhodium(I)] (65 mg) was heated for 3 h with bromobenzene (40 ml). Work-up in the usual way afforded the phenylrhodium(III) azaporphyrin (23 mg, 43%) and only a trace of the corresponding benzoylrhodium-(III) derivative.

n-Butoxycarbonylrhodium(III) *Etioporphyrin I* (6a; R^3 = Bu^n).—μ-Etioporphyrinato-bis[dicarbonylrhodium(I)] (80 mg) was heated with freshly distilled n-butyl formate (3 ml) at 110 °C for 16 h. The excess of formate ester was then removed under reduced pressure and the residue purified by preparative t.l.c. The *product* (29 mg, 42.5%) formed orange-red plates from chloroform–light petroleum, m.p. >300° (Found: C, 65.5; H, 6.65; N, 8.25. $C_{37}H_{45}N_4O_2Rh$ requires C, 65.3; H, 6.65; N, 8.25%), *m/e* 680 (M^+) and 579 ($M - CO_2Bu$).

Benzyloxycarbonylrhodium(III) *Etioporphyrin I* (6a; R^3 = $PhCH_2$).—(*a*) Prepared as above from μ-etioporphyrinato-bis[dicarbonylrhodium(I)] (50 mg) and freshly distilled benzyl formate, this *product* (18 mg, 40%) formed red plates from chloroform–light petroleum, m.p. >300° (Found: C, 65.35; H, 5.95; N, 7.65; $C_{40}H_{43}N_4O_2Rh,H_2O$ requires C, 65.55; H, 6.2; N, 7.65%), *m/e* 714 (M^+), 686 ($M - CO$), and 670 ($M - CO_2$).

(*b*) μ-Etioporphyrinato-bis[dicarbonylrhodium(I)] (80 mg) was heated at 110 °C for 20 h with freshly distilled benzyl acetoacetate (3 ml). The product (16 mg, 22%), isolated in the usual way, was identical with that described above.

Ethoxycarbonylrhodium(III) *Etioporphyrin I* (6a; R^3 = Et).—Prepared (110 °C; 8 h) as above from μ-etioporphyrinato-bis[dicarbonylrhodium(I)] (80 mg) and ethyl acetoacetate (3 ml), this *product* (28 mg, 24.5%) formed purple plates from chloroform–light petroleum, m.p. >300° (Found: C, 61.95; H, 6.05; N, 7.95. $C_{35}H_{41}N_4O_2Rh,H_2O$ requires C, 62.7; H, 6.15; N, 8.35%); *m/e* 652 (M^+) and 579 ($M - CO_2Et$).

n-Propoxycarbonyl- and n-Propyl-rhodium(III) 3,7,13,17-*Tetraethyl*-2,8,12,18-*tetramethyl*-5-*azaporphyrin* (6b; R^3 = Pr^n) *and* (3b; R^3 = Pr^n).—μ-3,7,13,17-Tetraethyl-2,8,12,18-tetramethyl-5-azaporphyrinato-bis[dicarbonylrhodium(I)] (155 mg) was boiled under reflux in n-propyl formate (100 ml) containing anhydrous potassium carbonate (4 g) for 3 days. The excess of formate ester was removed under reduced pressure and the residue chromatographed (Kieselgel; benzene). The slower moving red band afforded, after work-up, the *n-propoxycarbonylrhodium*(III) *azaporphyrin* (71 mg, 57%), m.p. >300° (decomp. from 105°), red plates from acetone–methanol (Found: C, 63.25; H, 6.5; N, 10.35. $C_{35}H_{42}N_5O_2Rh$ requires C, 62.95; H, 6.35; N, 10.5%), *m/e* 667 (M^+) and 580 ($M - CO_2Pr$); τ 0.74 (2 H, s, *meso*-H), 0.98 (1 H, s, *meso*-H), 6.0 (4 H, m, CH_2Me), 6.38 (4 H, q, CH_2Me), 6.62 (6 H, s, Me), 6.78 (6 H, s, Me), 8.15 (t, 6 H, CH_2Me), 8.42 (6 H, t, CH_2Me), 9.51 (2 H, t, $CO_2{\cdot}CH_2Et$), and 11.57 (5 H, m, $CO_2{\cdot}CH_2Et$). The faster moving band was further separated by preparative t.l.c. and gave starting material (7 mg) and the *n-propylrhodium*(III) *azaporphyrin* (15 mg, 13%); *m/e* 623 (M^+), 609, 595, and 580 ($M - C_3H_7$), τ 0.33 (2 H, s, *meso*-H), 0.40 (1 H, s, *meso*-H), 6.13 (8 H, m, CH_2Me), 6.53 (6 H, s, Me), 6.59 (6 H, s, Me), 8.18 (12 H, m, CH_2Me), 11.99 (3 H, t, $RhCH_2{\cdot}CH_2Me$), 14.95 (2 H, m, $RhCH_2{\cdot}CH_2Me$), and 16.65 (2 H, m, $RhCH_2{\cdot}CH_2Me$).

Cyclopropylcarbonylmethylrhodium(III) *Etioporphyrin* I (8a; R^3 = cyclopropyl).—μ-Etioporphyrinato-bis[dicarbonylrhodium(I)] (100 mg) was suspended in freshly distilled cyclopropyl methyl ketone (3 ml) and the mixture heated at 110 °C for 20 h. Chromatography (neutral Al_2O_3; $CHCl_3$) gave the *product* (69 mg, 83%), which crystallised from chloroform–light petroleum as red needles, m.p. >300°

(Found: C, 65.15; H, 6.55; N, 8.25. $C_{37}H_{43}N_4ORh$ requires C, 65.35; H, 6.65; N, 8.25%), *m/e* 662 (M^+) and 579 (M − CH_2·CO–cyclopropyl); $\nu_{max.}$ 1 670 cm^{-1}; τ 0.63 (4 H, s, *meso*-H), 6.26 (8 H, q, CH_2Me), 6.70 (12 H, s, Me), 8.31 (12 H, t, CH_2Me), 11.20 (2 H, m, cyclopropyl), 11.64 (2 H, m, cyclopropyl), 14.10 (1 H, m, cyclopropyl), and 16.05 (2 H, d, $J_{Rh,H}$ 4.3 Hz, $RhCH_2$).

Benzoylmethylrhodium(III) *Etioporphyrin I* (8a; R^3 = Ph).—μ-Etioporphyrinato-bis[dicarbonylrhodium(I)] (100 mg) was heated at 110 °C for 4 h in acetophenone (2 ml). The mixture was chromatographed (neutral Al_2O_3; $CHCl_3$) and then further purified by preparative t.l.c. ($CHCl_3$–light petroleum, 1 : 1). The *product* (40 mg, 45%) formed red prisms from chloroform–light petroleum, m.p. >300° (Found: C, 68.5; H, 6.25; N, 7.75. $C_{40}H_{43}N_4ORh$ requires C, 68.75; H, 6.2; N, 8.0%); *m/e* 698 (M^+) and 579 (M − $PhCOCH_2$); $\nu_{max.}$ 1 655 cm^{-1}; τ 0.63 (4 H, s, *meso*-H), 3.13 (1 H, t, *para* ArH), 3.67 (2 H, t, *meta* ArH), 6.06 (2 H, d, *ortho* ArH), 6.25 (8 H, q, CH_2Me), 6.70 (12 H, s, Me), 8.28 (12 H, t, CH_2Me), and 15.46 (2 H, d, $J_{Rh,H}$ 3.8 Hz, $RhCH_2$).

2-*Furoylmethylrhodium*(III) *Etioporphyrin I* (8a; R^3 = 2-furyl).—This was prepared (120 °C; 24 h) as above from μ-etioporphyrinato-bis[dicarbonylrhodium(I)] (100 mg) and freshly distilled 2-furyl methyl ketone (2 ml). Column chromatography (neutral Al_2O_3, $CHCl_3$) followed by preparative t.l.c. (chloroform–benzene, 1 : 1) gave the *product* (18 mg, 21%) as red plates from ether–light petroleum, m.p. 237—239° (Found: C, 66.75; H, 6.0; N, 8.0. $C_{38}H_{41}N_4O_2Rh$ requires C, 66.25; H, 6.0; N, 8.15%); $\nu_{max.}$ 1 650 cm^{-1}; τ 0.65 (4 H, s, *meso*-H), 3.50, 3.58, and 4.61 (3 × 1 H, all m, furyl H), 6.21 (8 H, q, CH_2Me), 6.65 (12 H, s, Me), 8.28 (12 H, t, CH_2Me), and 15.62 (2 H, m, $RhCH_2$).

1-*Benzoylethylrhodium*(III) *Etioporphyrin I* (9).—μ-Etioporphyrinato-bis[dicarbonylrhodium(I)] (100 mg) was treated (120 °C; 5 h) as above with ethyl phenyl ketone (2 ml). Work-up by column chromatography and preparative t.l.c. (chloroform–benzene, 1 : 1) afforded the *product* (21 mg, 23%), which formed red needles from chloroform–ether, m.p. >300° (Found: C, 68.45; H, 6.35; N, 7.65. $C_{41}H_{45}N_4ORh,0.5H_2O$ requires C, 68.25; H, 6.4; N, 7.75%); $\nu_{max.}$ 1 655 cm^{-1}; τ 0.21 (4 H, s, *meso*-H), 2.90 (1 H, t, *para* ArH), 3.36 (2 H, t, *meta* ArH), 5.42 (2 H, d, *ortho* ArH), 6.07 (8 H, q, CH_2Me), 6.52 (12 H, s, Me), 8.16 (12 H, t, CH_2Me), 13.50 (1 H, m, $RhCH$), and 15.00 (3 H, m, $RhCHMe$).

Cyclopropylcarbonylmethylrhodium(III) 3,7,13,17-*Tetraethyl*-2,8,12,18-*tetramethyl*-5-*azaporphyrin* (8b; R^3 = *cyclopropyl*).—Prepared in a similar manner (overnight; 110 °C) to the corresponding etioporphyrin complex from μ-3,7,13,17-tetraethyl-2,8,12,18-tetramethyl-5-azaporphyrinato-bis[dicarbonylrhodium(I)] (100 mg) and cyclopropyl methyl ketone (25 ml). Preparative t.l.c. (benzene) afforded 3 red fractions of which the lowest R_F material was the *cyclopropylcarbonylmethylrhodium*(III) *derivative* (52 mg, 62%), m.p. >300 °C (decomp. from 150 °C), red plates from acetone–light petroleum (Found: C, 63.15; H, 6.25; N, 10.65. $C_{36}H_{42}N_5ORh,H_2O$ requires C, 63.4; H, 6.5; N, 10.3%), *m/e* 663 (M^+), 649, 637, 595, 580 (M − CH_2·CO–cyclopropyl); $\nu_{max.}$ 1 670 and 1 645br cm^{-1}; τ 0.60 (2 H, s, *meso*-H), 0.87 (1 H, s, *meso*-H), 5.99 (4 H, m, CH_2Me), 6.32 (4 H, q, CH_2Me), 6.56 (6 H, s, Me), 7.62 (6 H, s, Me), 8.13 (6 H, t, CH_2Me), 8.40 (6 H, t, CH_2Me), 11.0 (2 H, m, cyclopropyl), 11.47 (2 H, m, cyclopropyl), 13.78 (1 H, m, cyclopropyl), and 15.88 (2 H, d, $J_{Rh,H}$ 4.5 Hz, $RhCH_2$),

The material isolated from the fastest moving red band (3 mg) showed, in its n.m.r. spectrum, a doublet ($J_{Rh,H}$ 3.2 Hz) at τ 16.4, and is tentatively identified as methylrhodium(III) 3,7,13,17-tetraethyl-2,8,12,18-tetramethyl-5-azaporphyrin.

The other red band afforded acetylrhodium(III) 3,7,13,17-tetraethyl-2,8,12,18-tetramethyl-5-azaporphyrin (6 mg), identified by spectral comparison (n.m.r.) with an authentic sample.[1] This material was contaminated (n.m.r.) with a trace of a product identified as the cyclopropylcarbonylrhodium(III) azaporphyrin which showed signals for a cyclopropyl group at τ 12.0 (2 H, m), 12.5 (2 H, m), and 14.8 (1 H, m). The mass spectrum of this impure product contained peaks at *m/e* 649 [M^+ for the cyclopropanoylrhodium(III) azaporphyrin], 623 [M^+ for the acetylrhodium(III) azaporphyrin], and 580 [rhodium(III) azaporphyrin].

3-(p-*Fluorobenzoyl*)*propylrhodium*(III) *Etioporphyrin I* (10; R^1 = Me, R^2 = *p* = FC_6H_4),—Prepared (110 °C; 4.5 h) from μ-etioporphyrinato-bis[dicarbonylrhodium(I)] (100 mg) and cyclopropyl *p*-fluorophenyl ketone (3 ml). Column chromtography (neutral Al_2O_3; chloroform–light petroleum) gave a fraction which afforded the *product* (30 mg, 32%) as red plates from chloroform–light petroleum, m.p. 222—224° (Found: C, 68.15; H, 6.65; F, 2.35; N, 7.9. $C_{42}FH_{46}N_4ORh$ requires C, 67.75; H, 6.2; F, 2.55; N, 7.5%); $\nu_{max.}$ 1 680 cm^{-1}; τ 0.42 (4 H, s, *meso*-H), 3.30 (4 H, m, ArH), 6.16 (8 H, q, CH_2Me), 6.62 (12 H, s, Me), 8.27 (12 H, t, CH_2Me), and 11.18, 14.90, and 16.15 (3 × 2 H, all m, $RhCH_2$·CH_2·CH_2).

Ethoxycarbonylmethylrhodium(III) *Etioporphyrin I* (8a; R^3 = OEt).—μ-Etioporphyrinato-bis[dicarbonylrhodium(I)] (85 mg) was heated at 110 °C for 30 min in a mixture of ethyl bromoacetate (4 ml) and anhydrous potassium carbonate (500 mg) during which time the brown solution slowly turned red. The excess of ethyl bromoacetate was removed under reduced pressure and the residue dissolved in chloroform and washed with water; the dried (Na_2SO_4) chloroform solution was evaporated to dryness and the residue was separated by preparative t.l.c. After further t.l.c. the *product* (15 mg, 21%), m.p. >300°, was obtained as red plates from chloroform–light petroleum (Found: C, 64.65; H, 6.45; N, 8.4. $C_{36}H_{43}N_4O_2Rh$ requires C, 64.85; H, 6.5; N, 8.4%), *m/e* 666 (M^+) and 579 (M − CH_2·CO_2Et); $\nu_{max.}$ 1 710 cm^{-1}; τ 0.33 (4 H, s, *meso*-H), 6.10 (8 H, q, CH_2Me), 6.53 (12 H, s, Me), 8.19 (12 H, t, CH_2Me), 8.52 (2 H, q, O·CH_2Me), 9.96 (3 H, t, O·CH_2·*Me*), and 16.01 (2 H, d, $J_{Rh,H}$ 5 Hz, $RhCH_2$).

Rhodium(III) *Etioporphyrin I Iodide* (14).—(*a*) Iodine (6.4 mg, 2.04 mol) was added to a solution of μ-etioporphyrinato-bis[dicarbonylrhodium(I)] (10 mg) in chloroform (2 ml). The brown solution changed colour to bluish green, then red, and after 15 min was chromatographed (silica; chloroform). The red eluate afforded the *iodide* (14) (8 mg, 71%), m.p. >300° (darkened at 150°), as purple plates from chloroform–light petroleum (Found: C, 53.2; H, 5.25; I, 17.8; N, 7.45. $C_{32}H_{36}IN_4Rh,H_2O$ requires C, 53.05; H, 5.3; I, 17.5; N, 7.75%), *m/e* 706 (M^+) and 579 (M − I), τ −0.17 (4 H, s, *meso*-H), 5.90 (8 H, q, CH_2Me), 6.33 (12 H, s, Me), and 8.11 (12 H, t, CH_2Me).

(*b*) A solution of di-μ-chloro-bisdicarbonylrhodium (1 g) in chloroform (100 ml) was added to a solution of etioporphyrin I (1 g) in chloroform (100 ml) containing an excess of sodium acetate. The solution was kept at room temperature for 2 h. The inorganic salts were then filtered off, iodine (640 mg, 2 mol) was added, and the solution was kept for 1 h. T.l.c. then showed that some rhodium(I) complex

was still present. More iodine (320 mg, 1 mol) was added and the mixture kept for a further 1 h at room temperature. The chloroform was then removed under reduced pressure and the residue chromatographed on neutral alumina (chloroform). Evaporation of the red eluate and crystallisation of the residue from chloroform–light petroleum gave, in two crops, purple plates of rhodium(III) etioporphyrin I iodide (987 mg, 57%), m.p. >300°.

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