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STRUCTURE AND REACTIVITY OF Rh(I) COMPLEXES OF POLYPYRROLE MACROCYCLES AND THEIR N-ALKYLATED DERIVATIVES

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We recently reported the preparation of several out-of-plane $Rh(CO)_2$ complexes of polypyrrole macrocycles and showed that the porphyrin complexes undergo oxidative addition reactions with alkyl halides, carboxylic acid anhydrides and benzoyl chloride.[1,2] A number of examples of formal insertion into the α-CH bond of ketones were also reported.[2] Rh(I) complexes, in particular $(PPh_3)_3RhCl$, have proved useful reagents for the decarbonylation of aldehydes to the corresponding hydrocarbon,[3,4] and these reactions are thought to involve intermediate acylrhodium(III) hydrides (eg. 1). Acyl intermediates have been isolated from the related Rh(I) catalysed decarbonylation of acyl halides,[3] but not from the analogous decarbonylation of aldehydes. We now report the isolation of stable acylrhodium(III) complexes from reactions of aldehydes with Rh(I) porphyrin complexes. Thus (2a) reacts with benzaldehyde (110°/20 hr) to give (3a; R^2 = Ph; 43.5%) and (4a; R^2 = Ph; 7.5%). Valeraldehyde (110°/5 hr) similarly gives (3a; R^2 = n-C_4H_9; 33.5%) and only a trace amount of the butylrhodium(III) complex. The azaporphyrin (2b)[5] reacts with benzaldehyde (C_6H_6, 80°, 3 dy) to give (3b; R^2 = Ph; 18%) and (4b; R^2 = Ph; 54%).

The dirhodium complexes (2a and b) have also been found to undergo oxidative addition reactions with aryl halides together with a varying amount of insertion of carbon monoxide. Thus (2a) reacts with bromobenzene to give (3a; R^2 = Ph; 14%) and (4a; R^2 = Ph; 18%). In contrast the azaporphyrin (2b) reacts (100-110°, 3 hr) to give (4b; R^2 = Ph; 43%) and only a trace of the benzoyl rhodium(III) complex. Addition of iodine to a chloroform solution of (2a) at room temperature rapidly gives the "normal" Rh(III) porphyrin (4a, R^2 = I, 71%).

$Rh_2(CO)_4Cl_2$ reacts with both N(21)- and N(22)-methylcorroles to give essentially quantitative yields of complexes containing only one $Rh(CO)_2$ moiety in accord with our previous observations on N-unsubstituted corroles.[1] The $Rh(CO)_2$ complex of 8,12-diethyl-2,3,7,13,17,18,22-heptamethylcorrole is a mixture of two monorhodium complexes (4:1 , nmr). The N(21)-methylcorrole complex and the major complex from the N(22)-methylcorrole are formulated as (5a and b). A single crystal X-ray structure of the N(21)-isomer unequivocally establishes its structure as (5a) and shows that the $Rh(CO)_2$ and methyl moieties are trans and that the corrole ring is considerably distorted (fig.).

A previous example of the reaction of an N-alkylated porphyrin with $Rh_2(CO)_4Cl_2$ formulated the resulting complex as (6).[6] However an alternative structure (7) appears possible for this product. Structure (7) is analogous to $Rh(CO)_2$ complexes of other polypyrrole macrocycles containing only one inner pair of imino (=N-)/amino(NH) nitrogen atoms (corroles, thiaphlorins).[1] The salt formulation (7) would also accord with the enhanced basicity of N-alkyl porphyrins[7] and porphyrin salts with the $[Rh(CO)_2Cl_2]^-$ anion are known.[8] Under our standard conditions $[Rh_2(CO)_4Cl_2/CHCl_3/NaOAc/RT]$ N-methyl etioporphyrin I gave the methylrhodium (III) complex (4a; R^2=Me; 83%). When the reaction was carried out in the presence of excess ethyl iodide a mixture (50:50) of methyl- and ethyl-rhodium(III) complexes (4a; R^2=Me or Et; 56%) was obtained.

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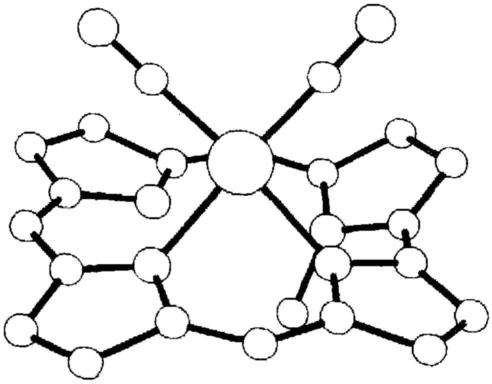
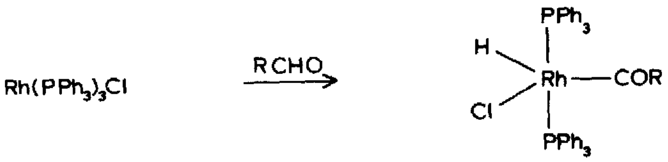
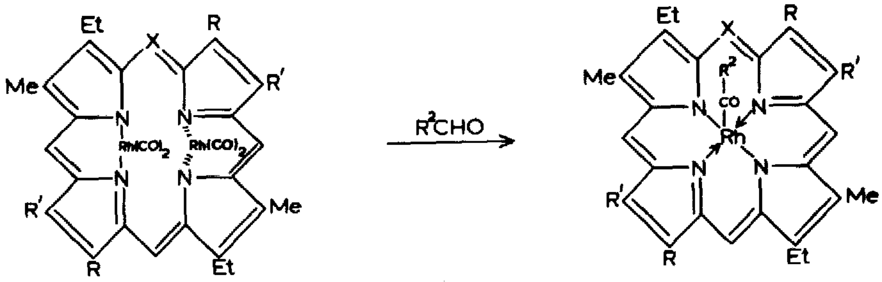


Fig. $Rh(CO)_2$ complex (5a) (β-substituents omitted for clarity)



(1)

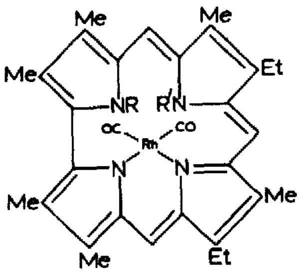


(a) R = Me, R' = Et, X = CH

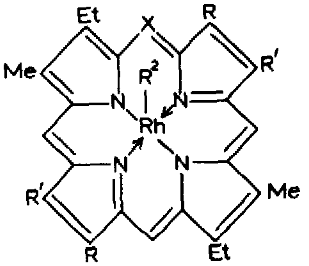
(b) R = Et, R' = Me, X = N

(2)

(3)



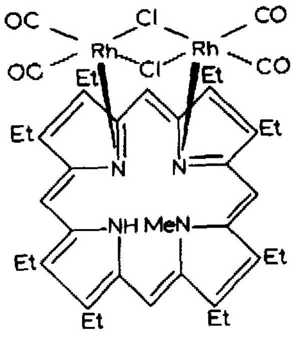
(5)



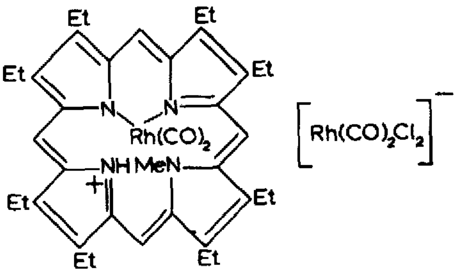
(4)

(a) R = Me, R' = H, X = CH

(b) R = H, R' = Me, X = N



(6)



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