RHODIUM (I) COMPLEXES OF POLYPYRROLE MACROCYCLES

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It was recently reported that octaethylporphyrin reacts with $Rh_2(CO)_4Cl_2$ to give a dirhodium chloro bridged complex [1] A later X-ray study[2] revealed the absence of chlorine and the trans arrangement of the two rhodium atoms (I; R=Et). We have devised an improved method for preparing (1; R=Et) and related rhodium complexes of other polypyrrole macrocycles. A chloroform solution of $Rh_2(CO)_4Cl_2$ is added to a solution of the macrocycle in chloroform containing excess anhydrous sodium acetate.   After keeping at room temperature for 10-30 mins the mixture is washed with water, dried and chromatographed on alumina or silica. The following dirhodium tetracarbonyl complexes were prepared in this way: etioporphyrin I (98%), octaethylporphyrin (98%), deuteroporphyrin IX (88%), and protoporphyrin IX (97%).   All the new dirhodium complexes are analogous to (I) and the complexes from deuteroporphyrin IX and protoporphyrin IX are mixtures of two isomers (nmr). In contrast to the porphyrins 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole gives a mixture of products one of which is the monorhodium complex (2; 36%).   The assignment of the bridging rhodium atom to rings A/B rests on the unsymmetrical nature of the nmr spectrum $(CDCl_3)$ which has meso-proton signals at 0.61, 0.81 and 0.83 τ and shows a similar characteristic upfield shift of signals of β-substituents of the metallated rings as has been observed for N-alkylated rings.[3,4] The meso-thiaphlorin (3)[4] also reacts under the same conditions as porphyrins to give a monorhodium complex (4; 76%). Microanalysis confirms the retention of sulphur in (4) and the nmr spectrum $(CDCl_3)$ establishes that the macrocycle has not undergone oxidation to the meso-thiaporphyrin since it exhibits meso-proton signals at 1.40, 2.50 and 3.50 τ. Imino proton signals are observed at 1.56 and 4.16 τ and once again the

characteristic upfield shift of the signals of the β-substituents of the metallated rings occurs.

The alternative structures for the corrole and thiaphlorin macrocycles involving rhodium bridging of rings A and C (e g. 5) appear less likely. Porphyrins undergo di-N-alkylation on adjacent rings rather than di-N-alkylation on rings A and C[5], and corroles are thought to undergo di-N-alkylation on rings A and B.[3] The nmr of (4) shows a marked downfield shift of one meso-proton signal compared to the parent macrocycle which has meso-proton signals at 2.48 (2H) and 3.73 (1H) τ. This shift is best accommodated by structure (4) rather than (5). Molecular ions are observed in the mass spectra of all the porphyrin complexes, except the protoporphyrin IX complex, if the spectra are determined at about 180° Higher temperatures result in the non-observance of the molecular ion The porphyrin complexes show a strong fragment ion corresponding to M-2CO and M+4 ions are observable under certain conditions.

The dirhodium porphyrin complexes undergo oxidative addition and insertion reactions with alkylating agents Thus (1; R=Me) reacts with methyl iodide at room temperature over 4 days to give a mixture of the rhodium (III) complexes (6; R=Me or COMe) together with a third unidentified product. Trideuteriomethyl iodide gives the corresponding deuteriated products. A similar result was obtained with ethyl iodide which gave (6; R=Et or COEt). In both cases no significant amount of "ordinary" Rh(III) porphyrin complexes (i.e 6, R=I or OH) were produced. When methyl or ethyl fluorosulphonate were used as alkylating agents a faster reaction (24 hr) ensued but more complex mixtures were produced. However the respective alkyl- and acyl-Rh(III) porphyrin complexes were again produced. The acetyl Rh(III) porphyrin complex (6; R=COMe) was also obtained when (1; R=Me), dissolved in acetic acid containing a little chloroform and excess sodium acetate, was heated on a steam bath for 17 hr. The only other product from this reaction was Rh(III) etioporphyrin acetate. The source of the carbonyl moiety in (6; R=COMe) is under study.
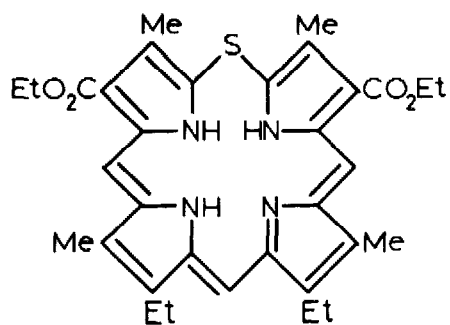
The alkyl- and acyl-Rh(III) complexes have characteristic spectra. Thus (6; R=COMe) exhibits an ir band at 1725 cm^{-1}, an nmr signal (CDCl$_3$) at 13.6 τ (Rh-CO-Me) and has a strong M-43 ion in its mass spectrum. The methyl derivative (6; R=Me) has an nmr signal (CDCl$_3$) at 16.56 τ (J_{Rh-H} = 2.3 Hz).
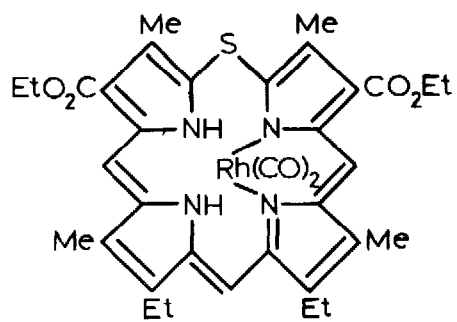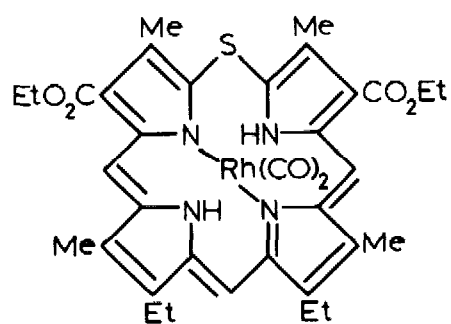
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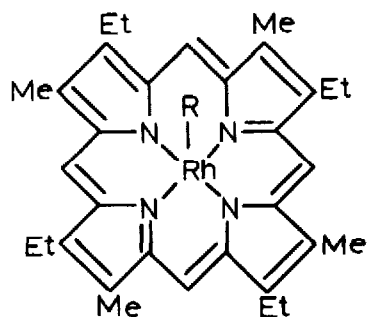
(4)

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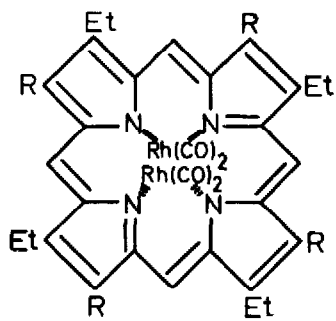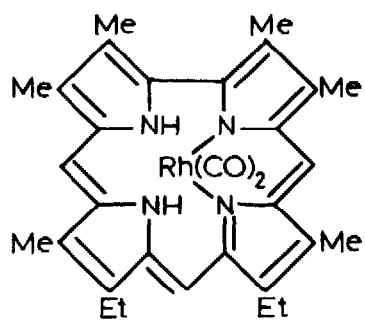
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