Dicarbonylrhodium(I) Complexes of Polypyrrole Macrocycles. Part 3.[1] Synthesis and Crystal Structures of Complexes of *N*-Methylcorroles, *N*-Methylporphyrins, and Acyclic Polypyrroles

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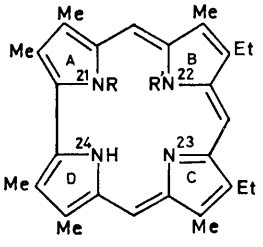
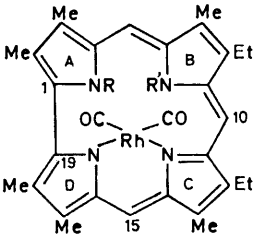
The reaction of di-μ-chloro-bis(dicarbonylrhodium) with *N*-methylcorroles gives stable out-of-plane complexes involving adjacent nitrogen atoms. An analogous complex is formed by a 21,24-dioxacorrole. The *N*-22-methylcorrole complex undergoes thermal equilibration with an isomeric complex involving non-adjacent nitrogen atoms. The *X*-ray crystal structures of two *N*-methylcorrolebis[dicarbonylrhodium(I)] complexes are reported. Reaction of di-μ-chloro-bis(dicarbonylrhodium) with *N*-methyletioporphyrin I gives rise to methylrhodium(III)–etioporphyrin and a similar reaction was observed with *N*-methylazaporphyrins. In the presence of an alkyl iodide, competitive alkylation of the rhodium occurs. Several examples of bis(dicarbonylrhodium) complexes of acyclic pyrrolic systems are reported including the first stable transition-metal complex of a 1,19-dideoxy-1,19-diunsubstituted biladiene-a,c.

THE reaction of di-μ-chloro-bis(dicarbonylrhodium) with polypyrrole macrocycles gives out-of-plane mono-[2] or bis-dicarbonylrhodium(I)[2,3] complexes depending on the number of imino- and amino-nitrogen atoms in the macrocycle. Thus each dicarbonylrhodium moiety requires one imino- and one amino-nitrogen atom for complexation. Corroles (1a) have three amino- and one imino-nitrogen atoms and form mono-dicarbonylrhodium(I) complexes formulated as (2a).[2] In all



(1) a; R = R' = H
b; R = Me, R' = H
c; R = H, R' = Me

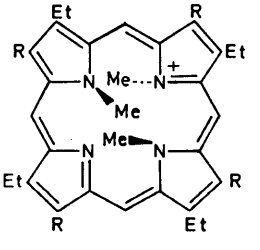


(2) a; R = R' = H
b; R = Me, R' = H
c; R = H, R' = Me

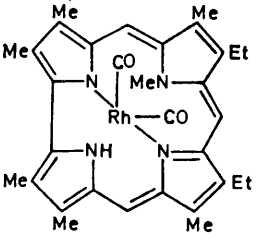
cases previously studied the complexation of the rhodium(I) moiety involved adjacent nitrogen atoms. A study of *N*-alkylated macrocycles was undertaken to see if this would result in complexation of rhodium by non-adjacent nitrogen atoms. This possibility was suggested by *N*-alkylation studies on porphyrins in which the *NN'N''*-trimethylporphyrins have the *trans,trans* arrangement (3).[4-6]

RESULTS AND DISCUSSION

The *N*-21-methylcorrole (1b) reacts with di-μ-chloro-bis(dicarbonylrhodium) in chloroform containing sodium acetate to give a monomeric dicarbonylrhodium complex (92%).[7] The *N*-methyl group in the product gave rise to an n.m.r. signal ($CDCl_3$) at τ 13.76 compared to a value of τ 13.01 in (1b) and the *meso*-proton signals also suffered an upfield shift on complexation, from τ 0.78, 0.96, and 1.1 to τ 0.84, 1.12, and 1.34. The signal at τ 1.34 is assigned to a *meso*-proton between the two pyrrole rings bonded to rhodium. *N*-Complexation of a $Rh(CO)_2$ moiety results in a selective upfield shift of the β-substituents of the ring containing the complexed nitrogen atom,[2] analogous to that observed on *N*-methylation of porphyrins.[4-6] The difference in chemical shift of the methyls of the ethyl groups in (1b) (Δτ 0.02) was accentuated on complexation (Δτ 0.1), thus implicating the *N*-22- or *N*-23-nitrogen atom in the co-ordination to rhodium. The *N*-21-nitrogen is unlikely to participate in the co-ordination to rhodium due to steric constraints, but a choice between the remaining 23,24-, 22,24-, and 22,23-bridged structures was not possible on spectroscopic evidence. However, *X*-ray crystallography (below) showed that the product was the 23,24-isomer (2b). The *N*-22-methylcorrole (1c) reacted rapidly (5 min) with an excess of di-μ-chloro-bis(dicarbonylrhodium) at room temperature (sodium acetate buffer). The product was a mixture of isomeric rhodium complexes (7 : 1) as shown by n.m.r. where the *N*-methyl region contained two methyl signals, at τ 14.69 (major isomer) and 15.46 (minor isomer). The two isomers were tentatively assigned structures (2c; major isomer) and (4; minor isomer). These assignments were based on the established structure (2b) for the *N*-21-methyl isomer, and on interpretation and comparison of the n.m.r. spectra with the spectra of the related tri-*N*-methylporphyrins (3). In particular the ring B *N*-methyl

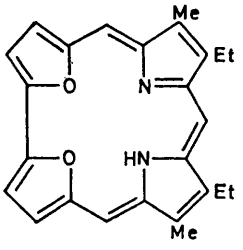


(3) a; R = Et
b; R = Me



(4)

group in (3a) or (3b) occurs at substantially higher field than any other *N*-methyl group in the mono-, di-, and tri-*N*-methylporphyrins; (3a), $\tau = 17.08$ [5] and (3b), $\tau = 17.06$.[6] This is due to the ' bowing ' of the molecule which occurs due to the steric repulsion of the two *cis*-methyl groups on rings A and C. This brings the ring B *N*-methyl group more into the centre of the ring current of the macrocycle. A similar situation would be expected in (4), whereas formation of (2c) would be expected to result in twisting about an axis through C(10) and the 1,19-direct link, and thus less shielding of the *N*-22-methyl than in (4). Inspection of the n.m.r. spectra also provides clear evidence for involvement of ring C in bonding to rhodium in both complexes since the spectra of the complexes show differential shielding of one β-ethyl group when compared with the n.m.r. spectrum of the uncomplexed macrocycle. The assigned structure (2c) [7] for the major isomer was confirmed by *X*-ray crystallography (below). The initial ratio (7 : 1) of (2c) : (4) altered to 4 : 1 when the reaction mixture was set aside for 24 h before work-up. The interconversion of (2c) and (4) was studied, using the 7 : 1 mixture, at 50 °C in [$^2H_6$]acetone by n.m.r. monitoring of the *N*-methyl signals of (2c) and (4). The equilibrium ratio of (2c) : (4) after 6 d was 13 : 16 which corresponds to a free-energy difference of 0.13 kcal mol^{-1}. The first-order rate constants were $k_1 = (1.6 \pm 0.1) \times 10^{-5}$ s^{-1} and $k_{-1} = (1.3 \pm 0.1) \times 10^{-5}$ s^{-1}. There are a number of possible mechanisms for the equilibration of (2c) and (4); *e.g.* a five-co-ordinate intermediate may be involved in which rhodium is bonded to N-21, N-23, and N-24. Breaking of the N-21 or N-24 bond with proton transfer then completes the interconversion. An attractive alternative involves oxidative–addition of the N–H bond to the co-ordinated Rh^{I} to give a Rh^{III}–H intermediate followed by a reductive–elimination regenerating the N–H at either N-21 or N-24. The *X*-ray crystal structure of (2c) (below) shows that the distance between N-21 (the unbonded nitrogen atom) and the rhodium atom is 3.04 Å, compared to an average Rh–N bond length of 2.059 Å for the covalently bonded nitrogen atoms. The Rh · · · H(N-21) distance is 2.50 Å assuming the hydrogen atom lies in the plane of the pyrrole ring and an N–H bond length of 0.86 Å. Thus no bonding interaction occurs between these two atoms.



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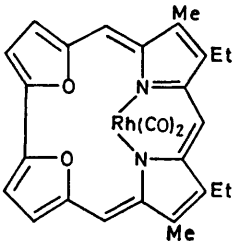


(6)

No 22,23-rhodium-bridged complexes were obtained from (1a—c), and it was thus of interest to study the reaction of the dioxacorrole (5) with di-μ-chloro-bis-(dicarbonylrhodium). The reaction was slow and gave a poor yield of the 22,23-rhodium-bridged complex (6) (23%). The n.m.r. spectrum of (5) reflects the symmetry of the molecule with equivalent methyl and ethyl groups and *meso*-proton signals at τ 0.53 (2 H) and 0.77 (1 H). In the rhodium complex (6) the methylene protons of the two ethyl groups give rise to an ABX_3 pattern whilst the remainder of the spectrum retains its symmetrical pattern with *meso*-proton signals at τ 0.30 (2 H) and 0.69 (1 H). The symmetrical nature of the n.m.r. spectrum and, in particular, the 2 : 1 pattern for the *meso*-proton signals accords with structure (6) rather than the alternative complex in which the rhodium atom bridges furan and pyrrole rings. The non-equivalence of the methylene protons of the ethyl groups in the n.m.r. spectrum of (6) may reflect restricted rotation arising from complexation of the macrocycle but is more probably due to the methylene protons becoming diastereotopic upon complexation of the bis(dicarbonylrhodium) moiety.

There has been considerable interest recently in out-of-plane metalloporphyrin complexes,[8] particularly in relation to the mechanism of metal insertion into porphyrins, and the *X*-ray crystal structure of the octaethylporphyrin analogue of (14) has been reported.[9]

TABLE 1

Fractional co-ordinates (× 10^4) with estimated standard deviation in parentheses for the *N*-21-methylcorrole complex

Atom	*x/a*	*y/b*	*z/c*
Rh(1)	3 355(1)	767(1)	572(1)
C(1)	2 907(9)	1 781(6)	−2 423(11)
C(2)	2 637(11)	2 577(6)	−2 265(12)
C(3)	1 919(1)	2 562(7)	−1 757(13)
C(4)	1 723(9)	1 764(7)	−1 563(11)
C(5)	1 127(9)	1 462(7)	−765(12)
C(6)	1 202(9)	748(7)	15(11)
C(7)	673(10)	469(7)	1 093(13)
C(8)	980(11)	−212(7)	1 677(13)
C(9)	1 692(11)	−345(6)	1 038(12)
C(10)	2 211(11)	−919(6)	1 317(13)
C(11)	2 926(10)	−991(6)	790(13)
C(12)	3 335(10)	−1 721(7)	662(15)
C(13)	4 010(11)	−1 546(7)	21(15)
C(14)	3 985(10)	−717(7)	−376(13)
C(15)	4 492(9)	−325(6)	−1 237(11)
C(16)	4 321(9)	401(6)	−1 859(11)
C(17)	4 686(10)	793(7)	−3 029(12)
C(18)	4 231(9)	1 410(7)	−3 425(12)
C(19)	3 634(9)	1 417(6)	−2 508(12)
N(21)	2 308(8)	1 311(5)	−2 033(9)
C(21)	2 170(10)	599(6)	−2 953(12)
N(22)	1 809(8)	252(5)	20(10)
N(23)	3 309(8)	−418(5)	124(9)
N(24)	3 715(7)	809(5)	−1 531(9)
C(25)	3 181(11)	3 290(7)	−2 452(15)
C(26)	1 528(10)	3 271(7)	−1 239(16)
C(27)	−43(10)	851(8)	1 489(13)
C(28)	599(12)	−699(8)	2 847(16)
C(29)	947(13)	−436(13)	4 314(17)
C(30)	3 058(10)	−2 543(8)	1 101(15)
C(31)	3 389(13)	−2 742(12)	2 508(25)
C(32)	4 630(10)	−2 095(8)	−360(19)
C(33)	5 443(11)	568(8)	−3 648(15)
C(34)	4 305(10)	1 969(8)	−4 717(13)
C(35)	3 070(11)	626(7)	2 464(14)
C(36)	3 426(9)	1 841(8)	853(12)
O(1)	2 946(8)	563(7)	3 648(10)
O(2)	3 457(7)	2 498(5)	1 067(11)

TABLE 2

Fractional co-ordinates of non-hydrogen atoms ($\times 10^4$) with estimated standard deviations in parentheses, for the *N*-22-methylcorrole complex

Atom	*x/a*	*y/b*	*z/c*
Rh(1)	4 744	2 280	1 921
C(1)	860(6)	3 171(5)	1 389(4)
C(2)	−290(6)	4 098(6)	1 473(5)
C(3)	−63(6)	4 543(5)	2 445(5)
C(4)	1 116(6)	3 892(5)	3 001(4)
C(5)	1 812(6)	3 987(4)	3 992(4)
C(6)	3 039(6)	3 295(4)	4 385(4)
C(7)	4 249(6)	3 582(4)	5 230(4)
C(8)	5 424(6)	2 775(5)	5 195(3)
C(9)	4 964(6)	1 922(4)	4 339(3)
C(10)	5 803(6)	967(4)	4 011(4)
C(11)	5 606(6)	312(4)	3 067(4)
C(12)	6 130(6)	−843(4)	2 807(4)
C(13)	5 563(6)	−1 173(4)	1 822(4)
C(14)	4 692(6)	−224(4)	1 470(4)
C(15)	3 769(7)	−173(5)	555(4)
C(16)	2 724(6)	716(5)	326(3)
C(17)	1 418(8)	718(6)	−472(4)
C(18)	549(7)	1 693(6)	−263(4)
C(19)	1 329(6)	2 314(5)	665(4)
N(21)	1 596(5)	3 081(4)	2 316(3)
N(22)	3 462(4)	2 230(3)	3 864(3)
C(22)	2 313(6)	1 311(5)	3 512(4)
N(23)	4 779(5)	684(3)	2 250(3)
N(24)	2 682(5)	1 724(4)	977(3)
C(25)	−1 341(8)	4 564(7)	660(6)
C(26)	−900(8)	5 548(6)	2 870(6)
C(27)	4 278(8)	4 651(5)	5 966(4)
C(28)	7 000(7)	2 806(5)	5 875(4)
C(29)	7 068(10)	2 248(10)	6 711(6)
C(30)	7 090(7)	−1 532(5)	3 519(5)
C(31)	8 792(9)	−1 253(7)	3 781(7)
C(32)	5 748(8)	−2 315(5)	1 200(5)
C(33)	1 030(9)	−239(7)	−1 335(4)
C(34)	−1 011(9)	1 999(8)	−852(5)
C(35)	6 656(7)	2 632(5)	2 748(4)
C(36)	4 616(7)	3 675(5)	1 526(4)
O(1)	7 839(5)	2 833(4)	3 245(4)
O(2)	4 548(7)	4 518(4)	1 279(4)

Comparatively few *X*-ray structures of corroles [10] and metallocorroles [11,12] have been determined and the current examples are the first out-of-plane complexes.

The essential features of the structures are the expected *trans* relationship of the *N*-methyl group and the bis(dicarbonylrhodium) moiety together with appropriate

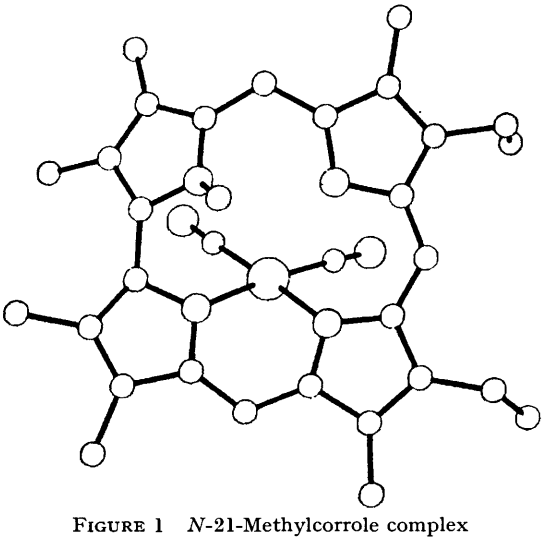


FIGURE 1 *N*-21-Methylcorrole complex

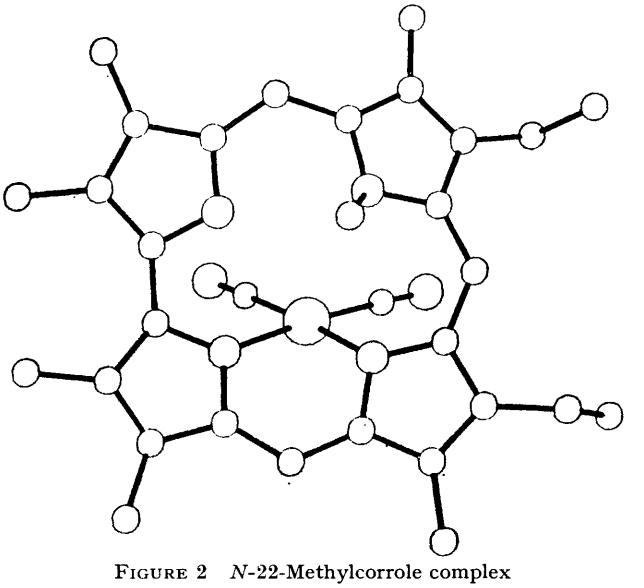


FIGURE 2 *N*-22-Methylcorrole complex

TABLE 3

Bond lengths (Å), with estimated standard deviations in parentheses

	21-Me complex	22-Me complex
C(1)–C(2)	1.446(16)	1.411(8)
C(1)–N(21)	1.396(18)	1.359(6)
C(1)–C(19)	1.456(22)	1.430(9)
C(2)–C(3)	1.384(19)	1.377(9)
C(2)–C(25)	1.571(20)	1.513(8)
C(3)–C(4)	1.415(17)	1.433(8)
C(3)–C(26)	1.480(18)	1.474(9)
C(4)–C(5)	1.410(19)	1.397(8)
C(4)–N(21)	1.382(17)	1.367(7)
C(8)–C(6)	1.420(16)	1.392(7)
C(6)–C(7)	1.469(19)	1.416(7)
C(6)–N(22)	1.385(17)	1.419(6)
C(7)–C(8)	1.393(18)	1.371(7)
C(7)–C(27)	1.496(21)	1.489(7)
C(8)–C(9)	1.439(20)	1.431(7)
C(8)–C(28)	1.534(18)	1.497(8)
C(9)–C(10)	1.378(20)	1.384(7)
C(9)–N(22)	1.405(14)	1.401(6)
C(10)–C(11)	1.391(23)	1.408(7)
C(11)–C(12)	1.449(17)	1.429(7)
C(11)–N(23)	1.349(16)	1.363(6)
C(12)–C(13)	1.394(20)	1.373(8)
C(12)–C(30)	1.541(13)	1.503(8)
C(13)–C(14)	1.459(16)	1.420(7)
C(13)–C(32)	1.503(21)	1.499(7)
C(14)–C(15)	1.428(18)	1.383(7)
C(14)–N(23)	1.359(17)	1.391(6)
C(15)–C(16)	1.396(15)	1.391(8)
C(16)–C(17)	1.440(17)	1.420(8)
C(16)–N(24)	1.335(17)	1.377(7)
C(17)–C(18)	1.383(19)	1.373(9)
C(17)–C(33)	1.536(21)	1.504(9)
C(18)–C(19)	1.380(18)	1.431(8)
C(18)–C(34)	1.538(15)	1.498(9)
C(19)–N(24)	1.384(13)	1.370(7)
N(21)–C(21)	1.502(13)	
N(22)–C(22)		1.482(6)
N(23)–Rh(1)	2.059(9)	2.048(4)
N(24)–Rh(1)	2.068(9)	2.062(4)
C(28)–C(29)	1.566(25)	1.478(10)
C(30)–C(31)	1.476(23)	1.513(10)
Rh(1)–C(35)	1.854(14)	1.843(6)
Rh(1)–C(36)	1.849(13)	1.850(6)
C(35)–O(1)	1.130(15)	1.130(6)
C(36)–O(2)	1.134(14)	1.125(7)

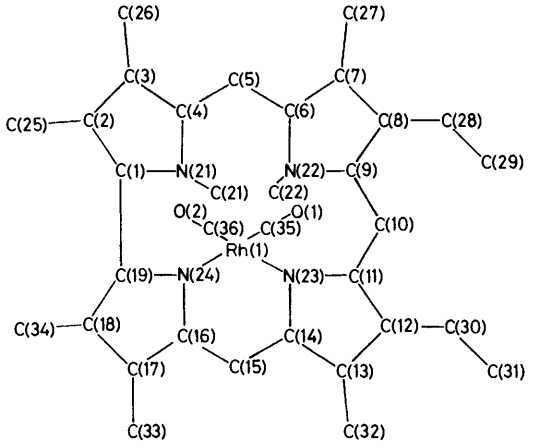


FIGURE 3 Crystallographic numbering

distortions of the pyrrole rings. The pyrrole rings are themselves essentially co-planar (Table 5) and the two pyrrole rings bound to rhodium are tilted towards the rhodium atom whilst the remaining two rings are displaced in the opposite direction (Table 6). In both (2b) and (2c) the maximum displacement occurs for the *N*-methylated ring and the minimum displacement for the remaining unco-ordinated ring. The average Rh–N bond length, 2.059 Å, is similar to that found for the related porphyrin complex (2.084 Å). The remaining two Rh · · · N distances are significantly different (Table 7) with the unmethylated ring showing the shorter Rh · · · N distance. The nitrogen atoms bearing

TABLE 4

Bond angles (°) with estimated standard deviations in parentheses

	21-Me complex	22-Me complex
C(2)–C(1)–N(21)	104(1)	105.4(5)
C(2)–C(1)–C(19)	135(1)	140.4(5)
C(19)–C(1)–N(21)	118(1)	114.1(5)
C(1)–C(2)–C(3)	110(1)	108.4(5)
C(1)–C(2)–C(25)	120(2)	127.6(7)
C(3)–C(2)–C(25)	130(1)	124.0(6)
C(2)–C(3)–C(4)	107(1)	108.6(5)
C(2)–C(3)–C(26)	123(1)	127.2(6)
C(4)–C(3)–C(26)	128(2)	124.2(7)
C(3)–C(4)–C(5)	128(1)	134.0(6)
C(3)–C(4)–N(21)	107(1)	104.1(5)
C(5)–C(4)–N(21)	124(1)	121.8(5)
C(4)–C(5)–C(6)	121(1)	124.9(5)
C(5)–C(6)–C(7)	124(1)	128.4(5)
C(5)–C(6)–N(22)	127(1)	123.0(5)
C(7)–C(6)–N(22)	109(1)	107.3(4)
C(6)–C(7)–C(8)	106(1)	108.5(4)
C(6)–C(7)–C(27)	127(1)	124.6(5)
C(8)–C(7)–C(27)	127(1)	126.6(6)
C(7)–C(8)–C(9)	109(1)	108.8(5)
C(7)–C(8)–C(28)	123(2)	126.9(5)
C(9)–C(8)–C(28)	128(1)	124.0(5)
C(8)–C(9)–C(10)	130(1)	128.2(5)
C(8)–C(9)–N(22)	108(1)	107.0(4)
C(10)–C(9)–N(22)	122(1)	124.8(4)
C(9)–C(10)–C(11)	129(1)	129.2(4)
C(10)–C(11)–C(12)	126(1)	127.0(5)
C(10)–C(11)–N(23)	125(1)	123.8(4)
C(12)–C(11)–N(23)	108(1)	109.1(4)
C(11)–C(12)–C(13)	108(1)	107.3(5)
C(11)–C(12)–C(30)	126(1)	124.2(5)
C(13)–C(12)–C(30)	126(1)	128.5(5)
C(12)–C(13)–C(14)	105(1)	107.5(4)
C(12)–C(13)–C(32)	129(1)	128.2(5)
C(14)–C(13)–C(32)	126(1)	124.3(5)
C(13)–C(14)–C(15)	123(2)	129.2(5)
C(13)–C(14)–N(23)	109(1)	108.2(4)
C(15)–C(14)–N(23)	127(1)	122.3(5)
C(14)–C(15)–C(16)	120(1)	125.1(5)
C(15)–C(16)–C(17)	128(1)	129.4(5)
C(15)–C(16)–N(24)	123(1)	121.7(4)
C(17)–C(16)–N(24)	108(1)	108.1(5)
C(16)–C(17)–C(18)	106(1)	107.4(5)
C(16)–C(17)–C(33)	126(1)	124.8(7)
C(18)–C(17)–C(33)	128(1)	127.6(6)
C(17)–C(18)–C(19)	108(1)	107.8(5)
C(17)–C(18)–C(34)	128(1)	126.1(6)
C(19)–C(18)–C(34)	123(1)	125.9(7)
C(18)–C(19)–C(1)	138(1)	134.5(5)
C(18)–C(19)–N(24)	109(1)	107.6(6)
C(1)–C(19)–N(24)	112(1)	115.6(4)
C(1)–N(21)–C(4)	111(1)	113.5(5)
C(1)–N(21)–C(21)	116(1)	
C(4)–N(21)–C(21)	120(1)	
C(6)–N(22)–C(9)	109(1)	108.1(4)
C(6)–N(22)–C(22)		119.1(4)
C(9)–N(22)–C(22)		116.9(4)
C(11)–N(23)–C(19)	109.4(10)	107.9(4)
C(11)–N(23)–Rh(1)	129.3(9)	127.8(3)
C(14)–N(23)–Rh(1)	113.7(9)	115.5(3)
C(16)–N(24)–C(19)	108.8(10)	108.9(4)
C(16)–N(24)–Rh(1)	117.5(8)	117.5(4)
C(19)–N(24)–Rh(1)	128.0(8)	130.6(4)
C(8)–C(28)–C(29)	107(1)	112.9(6)
C(12)–C(30)–C(31)	108(1)	112.4(5)
N(23)–Rh(1)–N(24)	81.6(3)	81.9(2)
N(23)–Rh(1)–C(35)	93.1(5)	93.3(2)
N(23)–Rh(1)–C(36)	176.1(5)	175.4(2)
N(24)–Rh(1)–C(35)	174.2(5)	174.5(2)
N(24)–Rh(1)–C(36)	94.5(4)	94.0(2)
C(35)–Rh(1)–C(36)	90.7(5)	90.7(3)
Rh(1)–C(35)–O(1)	175(2)	178.8(5)
Rh(1)–C(36)–O(2)	178(1)	179.2(6)

TABLE 5

Least-squares planes

Plane	Atoms	Maximum deviation of any atom from the mean plane (Å) (2b)	(2c)
1	C(1), C(4), C(5), C(6), C(9), C(10), C(11), C(14), C(15), C(16), C(19)	0.050	0.162
2	C(1), C(2), C(3), C(4), N(21)	0.025	0.024
3	C(6), C(7), C(8), C(9), N(22)	0.012	0.027
4	C(11), C(12), C(13), C(14), N(23)	0.033	0.015
5	C(16), C(17), C(18), C(19), N(24)	0.025	0.029

TABLE 6

Dihedral angles between planes (°)

	(2b)	(2c)
Planes 1 and 2	+30.5	+4.3
Planes 1 and 3	+9.4	+25.2
Planes 1 and 4	−18.9	−18.6
Planes 1 and 5	−15.4	−21.1

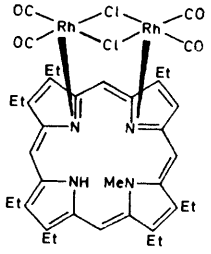
TABLE 7

Selected non-bonded distances (Å)

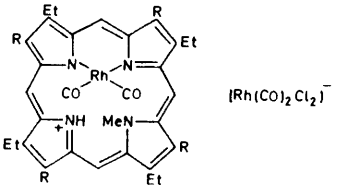
	(2b)	(2c)
Rh · · · N(21)	3.21	3.04
Rh · · · N(22)	2.97	3.29
N(21) · · · N(22)	2.78	2.76
N(22) · · · N(23)	2.94	3.09
N(23) · · · N(24)	2.70	2.69
N(21) · · · N(24)	2.72	2.60

the *N*-methyl substituents are sp^3 hybridised as shown by the N(21)–C(21) (1.502 Å) and N(22)–C(22) (1.482 Å) bond lengths. A similar situation was observed for an in-plane copper complex of (1b) which had an N–Me bond length of 1.54 Å.[11]

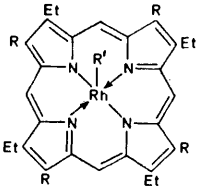
A previous report of the reaction of *N*-methyloctaethylporphyrin with di-μ-chloro-bis(dicarbonylrhodium) formulated the resulting complex as (7).[3] The data reported for this complex are also interpretable in terms of the alternative structure (8a). Attempts to chemically differentiate between (7) and (8a) were unsuccessful because of the facile conversion of the complex to the methylrhodium(III) complex (9a). I.r. studies on the



(7)



(8) a; R = Et
b; R = Me



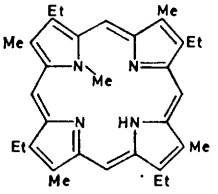
(9) a; R = Et, R' = Me
b; R = R' = Et
c; R = R' = Me
d; R = Me, R' = COMe
e; R = Me, R' = Et
f; R = Me, R' = COEt
g; R = Me, R' = CD_3
h; R = Me, R' = $COCD_3$

corresponding *N*-methyletioporphyrin complex [formulated as (8b)] also failed to provide definitive evidence to distinguish between (7) and (8). There is good reason, however, to favour the salt structure (8) for these complexes. Thus macrocycles containing one pair each of imino- and amino-nitrogen atoms, *e.g.* corroles,[2] thiaphlorins,[2] and other examples in this paper, are known to form monomeric dicarbonylrhodium(I) complexes. Protonation of such a complex [as in (8)] accords with the enhanced basicity of *N*-alkylporphyrins [4-6] and explains the behaviour of the complex on t.l.c. (SiO_2, $CHCl_3$) where it remains on the base line. Moreover, porphyrin salts with the $[Rh(CO)_2Cl_2]^-$ anion are known,[13] and di-μ-chloro-bis(dicarbonylrhodium) is known to undergo facile bridge cleavage.[14] The geometrical problem involved in bridging two adjacent nitrogen atoms in a porphyrin (interatomic distance *ca.* 2.75—2.95 Å) [15] by an Rh–$(\mu\text{-Cl})_2$–Rh moiety as in (7) is certainly not too severe since the porphyrin ring has an inherent flexibility as demonstrated by *N*-methylation studies.[4-6] Moreover, compounds containing the Rh–$(\mu\text{-Cl})_2$–Rh moiety show an ability to vary the Rh–Rh distance from 3.02 to 3.7 Å by varying the dihedral angle between the two $RhCl_2$ planes from *ca.* 65 to 0°.[16] However, varying the Rh–Rh distance will influence the interaction between the metal centres. It is generally considered that Rh–Rh distances of *ca.* 2.7 Å involve an electron-pair bond whilst Rh–Rh distances of *ca.* 3.1 and 3.5 Å involve weak interaction and no interaction, respectively. The complexes formulated as (8a and b) were diamagnetic as evidenced by their clean n.m.r. spectra and we favour structure (8) for these products.

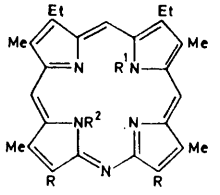
Ogoshi and his co-workers have reported the rearrangement of *N*-methyl- and *N*-ethyl-octaethylporphyrin complexes of di-μ-chloro-bis(dicarbonylrhodium) to the corresponding alkylrhodium(III) octaethylporphyrins (9a and b) in boiling chloroform or on chromatography on silica gel.[3] We observed analogous reactions in our studies of the reactions of *N*-methyletioporphyrin with di-μ-chloro-bis(dicarbonylrhodium), whereas we find that similar reactions do not occur with *N*-methylcorroles. Insertion of metal ions into *N*-alkylporphyrins [4,5,17,18] and -corroles [19] with formation of stable complexes retaining the *N*-alkyl group has been achieved with various divalent metal ions (Cu, Zn, Pd, Co, Ni, and Mn). In general, the metal complexes of *N*-methylporphyrins undergo demethylation by nucleophilic attack [17] apart from a cobalt(I) complex which undergoes a nitrogen-to-cobalt rearrangement giving the methylcobalt(III) porphyrin.[18] *N*-Methylcorrole metal complexes undergo thermal nitrogen-to-carbon rearrangements (Ni and Pd) or thermal cleavage to the metallocorrole (Cu).[19]

We have previously reported the oxidative addition of methyl and ethyl iodide to porphyrin- and azaporphyrin-bis[dicarbonylrhodium(I)] complexes to give a mixture of alkyl- and acyl-rhodium(III) porphyrin complexes [*e.g.* (9c and d)].[2] These reactions are slow and the acylrhodium(III) complex often predominates. It was of interest, therefore, to study the *N*-alkylporphyrins as precursors of alkylrhodium(III) porphyrins. We find that treating a chloroform solution of *N*-methyletioporphyrin I (10) with di-μ-chloro-bis(dicarbonylrhodium) in the presence of sodium acetate rapidly (2 h) gives the corresponding methylrhodium(III)–etioporphyrin I (9c) (83%) essentially free of the corresponding acetylrhodium(III) complex. Similar results were obtained with the *N*-methylazaporphyrins (11a and b) (1 : 1) [6] and (11c and d) (1 : 1) [6] which gave (12a) and (12b) respectively in moderate yield. Ogoshi and his co-workers have proposed that this type of process occurs by conversion of (7) to the corresponding *N*-alkylrhodium(I)–porphyrin [*e.g.* (13)] followed by migration of the methyl group from nitrogen to rhodium.[3] Our studies show that the reaction is sensitive to the solvent and that added alkylating agents can compete with the

N-alkyl group under our conditions. Thus when the reaction of (10) with di-μ-chloro-bis(dicarbonylrhodium) is carried out in the presence of an excess of ethyl iodide the product consists of a *ca.* 1 : 1 mixture of (9c) and

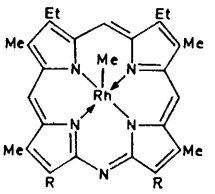


(10)



(11) a; R = Et, R^1 = H, R^2 = Me
b; R = Et, R^1 = Me, R^2 = H
c; R = R^2 = Me, R^1 = H
d; R = R^1 = Me, R^2 = H

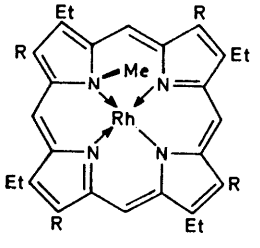
$Rh_2(CO)_4Cl_2$, $CHCl_3$, NaOAc



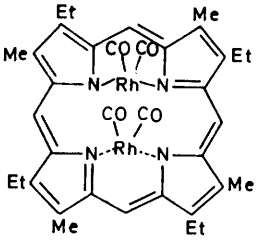
(12) a; R = Et
b; R = Me

(9e). A brief study of the reaction of (10) with di-μ-chloro-bis(dicarbonylrhodium) in the presence of excess of CD_3I revealed (Table 8) a variation in both rate and product composition as the solvent mixture was varied.

Thus under our conditions a wide variation in the ability of the ' external ' alkylating agent to compete with the *N*-methyl group has been observed. Increasing the ratio of $CHCl_3$ to CD_3I to 1 : 1 both slows the reaction and depresses the incorporation of the *N*-methyl group into the alkylrhodium(III)–porphyrin. Measurable amounts of carbonyl insertion products were also formed (Table 8). Moreover in some reactions small amounts of μ-etioporphyrinato-bis[dicarbonylrhodium-

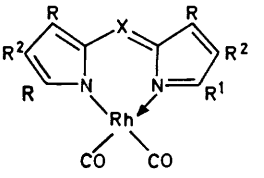


(13)

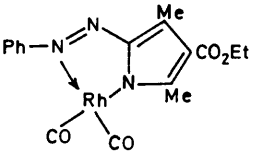


(14)

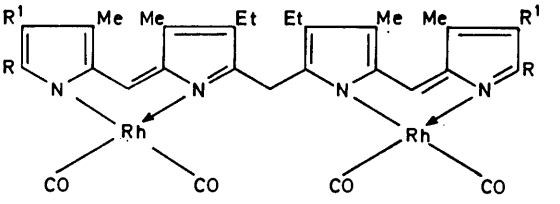
(I)] (14) [2] were detected on t.l.c. The incorporation fo the added alkylating agent into the alkylrhodium(III)–porphyrin might therefore arise *via* (14) whilst the retention of the original *N*-alkyl group in the alkylrhodium(III)–porphyrin might arise, as suggested previously, *via* (13).[3] Thus the factors which assist the



(15) a; X = CH, R = R^2 = Me, R^1 = H
b; X = N, R = R^1 = Ph, R^2 = H



(16)



(17) a; R = Me, R^1 = H
b; R = H, R^1 = Me

(presumably) nucleophilic removal of the *N*-alkyl group from *N*-alkylporphyrins would be expected to favour incorporation of added alkylating agent. However, the rate of these reactions is much faster than that observed for the reaction of (14) with methyl or ethyl iodide.[2]

TABLE 8

Reaction of (10) (10 mg) with di-μ-chloro-bis(dicarbonylrhodium) (10 mg) in the presence of an excess of anhydrous sodium acetate

Solvent composition/ml		Reaction	Molar ratio of products			Total
$CHCl_3$	CD_3I	time/h	(9c)	(9g)	(9d) + (9g)	yield/mg
0.5	1	7	33	7.25	5	8.2
0.5	3	10	7	1	1	9
2	2	16	Trace	9	4 [a]	15 [b]

[a] $RhCOCD_3$ with only a trace of $RhCOCH_3$. [b] 47% Of the product consisted of the salt (8b).

This observation suggests that di-μ-chloro-bis(dicarbonylrhodium) or some species derived from it accelerates the formation of alkylrhodium(III)–porphyrins. In accord with this we observe that addition of di-μ-chloro-bis(dicarbonylrhodium) to a solution of (14) in chloroform containing methyl or ethyl iodide and potassium carbonate accelerates the formation of alkylrhodium(III)–porphyrin. However, the rate is still slower than that observed for the corresponding reaction with *N*-methyletioporphyrin and, unlike the latter case, the product contains a substantial proportion of acylrhodium(III)–porphyrin.

The formation of bis[dicarbonylrhodium(I)] complexes is a general reaction for both cyclic and acyclic conjugated polypyrrolic systems containing at least one pair of amino- (NH) and imino-nitrogen atoms. Bis[di-

carbonylrhodium(I)] complexes of dipyrromethenes have been prepared by boiling a solution of the dipyrromethene hydrobromide, di-μ-chloro-bis(dicarbonylrhodium) and sodium acetate in benzene.[20] We find they are more conveniently and rapidly prepared in chloroform solution at room temperature. This procedure was used to prepare the representative examples (15a) and (15b). 2-Phenylazopyrroles form analogous complexes [*e.g.* (16)]. 1,19-Dideoxybiladienes-a,c contain two pairs of amino- and imino-nitrogen atoms and form complexes with di-μ-chloro-bis(dicarbonylrhodium) containing two bis[dicarbonylrhodium(I)] moieties, *e.g.* (17a and b). The complex (17b) is noteworthy in that formation of transition-metal complexes of 1,19-diunsubstituted-1,19-dideoxybiladienes-a,c usually results in concomitant cyclisation to the corresponding metallocorrole.[21] Co-ordination to the two bis(dicarbonylrhodium) moieties may sterically hinder the cyclisation process. However, we have been unable to prepare the corresponding rhodium-corroles by insertion of rhodium into the pre-formed macrocycle. Metal complexes [*e.g.* Co(II) and Ni(II)] of 1,19-dideoxy-1,19-dimethylbiladienes-a,c are well known.[22]

EXPERIMENTAL

General details were as described in previous papers in this series.

Dicarbonyl-(2,3,7,13,17,18,21-*heptamethyl*-8,12-*diethylcorrolato*)*rhodium*(I) (2b).—2,3,7,13,17,18,21-Heptamethyl-8,12-diethylcorrole [23] (50 mg) was dissolved in alcohol-free chloroform (50 ml). Anhydrous sodium acetate (500 mg) was added to the solution followed by di-μ-chloro-bis[dicarbonylrhodium(I)] (200 mg) and the mixture stirred for 2 h at room temperature. The resulting green solution (red fluorescence) was filtered through a short silica column, eluting with benzene. Evaporation of the solvent under reduced pressure gave the product as a purple solid (62 mg, 92%) which crystallised from acetone–methanol as purple plates, m.p. 240—242 °C (Found: C, 62.65; H, 5.75; N, 9.1. $C_{32}H_{35}N_4O_2Rh$ requires C, 62.94; H, 5.79; N, 9.18%); $\nu_{max.}$ 1 995 and 2 060 cm^{-1}; τ 0.83 (s, 1 H, *meso*-H), 1.12 (s, 1 H, *meso*-H), 1.34 (s, 1 H, *meso*-H), 6.35 (m, 4 H, CH_2Me), 6.72 (s, 3 H, Me), 6.86 (s, 3 H, Me), 6.88 (s, 3 H, Me), 6.97 (s, 3 H, Me), 7.03 (s, 3 H, Me), 7.05 (s, 3 H, Me), 8.32 (t, 3 H, CH_2*Me*), 8.43 (t, 3 H, CH_2*Me*), 10.73 (s, 1 H, NH), and 13.76 (s, 3 H, NMe).

Dicarbonyl-(2,3,7,13,17,18,22-*heptamethyl*-8,12-*diethylcorrolato*)*rhodium*(I) (2c).—2,3,7,13,17,18,22-Heptamethyl-8,12-diethylcorrole [23] (50 mg) was dissolved in alcohol-free chloroform (50 ml). Anhydrous sodium acetate (500 mg) was added to the solution followed by di-μ-chloro-bis[dicarbonylrhodium(I)] (200 mg) and the mixture stirred for 5 min at room temperature. The solution was then filtered through a short silica column, eluting with benzene. Evaporation of the solvent under reduced pressure gave a purple solid (49 mg, 73%) which was shown by n.m.r. spectroscopy to be a mixture of the 23,24-dicarbonylrhodium complex (2c) and the 21,23-dicarbonylrhodium complex (4) (7 : 1). Pure (2c) was obtained (22 mg, 33%) as purple plates on crystallisation of the solid from acetone–methanol, m.p. 218—220 °C (Found: C, 62.75; H, 5.70; N, 9.15. $C_{32}H_{35}N_4O_2Rh$ requires C, 62.94; H, 5.79; N, 9.18%); *m/e* 610 (M^+), 595, 554 ($[M - 2CO]^+$), and 539; τ 0.62 (s, 1 H, *meso*-H), 0.76 (s, 1 H, *meso*-H), 0.81 (s, 1 H, *meso*-H), 6.30 (m, 4 H, CH_2Me), 6.41 (s, 3 H, Me), 6.58 (s, 3 H, Me), 6.65 (s, 3 H, Me), 6.69 (s, 3 H, Me), 6.77 (s, 3 H, Me), 6.78 (s, 3 H, Me), 8.42 (t, 3 H, CH_2*Me*), 8.56 (t, 3 H, CH_2*Me*), 12.45 (s, 1 H, NH), and 14.69 (s, 3 H, NMe).

Kinetics of the Equilibration of the two isomeric Dicarbonylrhodium Complexes (2c) *and* (4).—An approximately 7 : 1 mixture (*ca.* 20 mg) of (2c) and (4), prepared as above, was dissolved in $(CD_3)_2CO$ (*ca.* 0.5 ml) and sealed in an n.m.r. tube. The tube was then placed in the heated (50 °C) probe of the n.m.r. spectrometer and a spectrum run every 15 min during 5 h. The tube was then heated outside the probe at 50 °C for a further 6 d and a final spectrum recorded. The relative concentrations of (2c) and (4) were taken to be proportional to the relative heights of the *N*-methyl signals for (2c) and (4). Both the forward and backward reactions in the equilibrium were assumed to be first order, as in equation (1). Modifying the standard

$$(2c) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (4) \qquad (1)$$

equation for the first-order reversible process [24] we obtain equation (2), where a = initial concentration of (2c), b = initial concentration of (4), x_t = amount of (2c) converted

$$-\ln(1 - x_t/x_e) = k_1[(a + b)t][b + x_e]^{-1} \qquad (2)$$

to (4) (mol l^{-1}) at time t, and x_e = amount of (2c) converted to (4) (mol l^{-1}) at equilibrium. The results are in Table 9.

TABLE 9

Time/h	*N*-Me Peak height (2c)	*N*-Me Peak height (4)	$-\ln(1 - x_t/x_e)$
0	17.3	7.8	0.000
0.25	17.8	8.1	0.004
0.50	17.8	8.1	0.004
0.75	18.3	8.5	0.025
1.00	18.9	9.0	0.052
1.25	18.1	9.0	0.093
1.50	18.1	9.0	0.093
1.75	17.8	9.3	0.146
2.00	18.2	9.5	0.146
2.25	17.9	9.8	0.201
2.50	17.8	9.7	0.196
2.75	17.1	9.7	0.243
3.00	18.2	10.4	0.255
3.25	17.3	10.1	0.282
3.50	17.1	10.3	0.322
3.75	17.0	10.4	0.345
4.00	17.1	10.6	0.364
4.25	16.7	10.6	0.395
4.50	16.7	10.6	0.395
4.75	16.6	10.9	0.446
5.00	16.3	11.0	0.458
∞	6.3	7.6	

A graph of $-\ln(1 - x_t/x_e)$ against t gave $k_1(a + b)(b + x_e)^{-1} = 0.1024$ h^{-1}; $k_1 = (1.6 \pm 0.1) \times 10^{-5}$ s^{-1} and $k_{-1} = (1.3 \pm 0.1) \times 10^{-5}$ s^{-1}.

Dicarbonyl-(8,12-*diethyl*-7,13-*dimethyl*-21,24-*dioxocorrolato*)*rhodium*(I) (6).—8,12-Diethyl-7,13-dimethyl-21,24-dioxocorrole (100 mg) [25] was dissolved in chloroform (50 ml). Di-μ-chloro-bis(dicarbonylrhodium) (100 mg) and an excess of anhydrous potassium carbonate were added and the mixture was set aside for 5 d at room temperature. The mixture was then washed with water, dried (Na_2SO_4), and chromatographed on silica eluting with chloroform.

Evaporation of the chloroform eluate and crystallisation of the residue from chloroform–light petroleum gave the *product* (33 mg; 23%) as purple prisms, m.p. 253—254 °C (Found: C, 59.4; H, 4.25; N, 5.07. $C_{27}H_{23}N_2RhO_4$ requires C, 59.78; H, 4.27; N, 5.16%); $\nu_{max.}$ 1 978 and 2 048 cm^{-1}; τ 0.30 (s, 2 H, *meso*-H), 0.47 (d, 2 H, furan-H), 0.69 (s, 1 H, *meso*-H), 0.72 (d, 2 H, furan-H), 6.20 (m, 4 H, CH_2Me), 6.67 (s, 6 H, Me), and 8.43 (t, 6 H, CH_2Me).

Reaction of N-*Methyletioporphyrin I with Di-μ-chloro-bis(dicarbonylrhodium).—Methylrhodium*(III)*–etioporphyrin* (9c). *N*-Methyletioporphyrin (20 mg) and di-μ-chloro-bis(dicarbonylrhodium) (20 mg) were dissolved in chloroform (5 ml) and an excess of anhydrous sodium acetate added. The mixture was set aside for 2 h, at room temperature and then washed with water, dried (Na_2SO_4), and chromatographed on alumina (eluting with chloroform). A small amount of μ-etioporphyrinato-bis[dicarbonylrhodium(I)] eluted first, followed by a red band which on work-up afforded the *product* (21 mg; 83%). The complex was identical with that described previously.[2]

Competitive Alkylations.—(*a*) *N*-Methyletioporphyrin (10 mg) was dissolved in chloroform (3 ml), and ethyl iodide (3 ml) and di-μ-chloro-bis(dicarbonylrhodium) (10 mg) added followed by an excess of anhydrous sodium acetate. The mixture was set aside for 3 h at room temperature and the product (13 mg) isolated in the usual way. The n.m.r. spectrum of the product showed it to be a 1 : 1 mixture of *methylrhodium*(III)– and *ethylrhodium*(III)*–etioporphyrin I.*

(*b*) Repetition of the above experiment using a reduced volume of ethyl iodide (1 ml) gave an alkylrhodium(III)–etioporphyrin mixture (11 mg), shown by n.m.r. spectroscopy to consist of a 3 : 2 mixture of *methylrhodium*(III)– and *ethylrhodium*(III)*–etioporphyrin I.*

Reaction of μ-Etioporphyrinato-bis[dicarbonylrhodium(I)*] with Alkyl Halides in the Presence of Di-μ-chloro-bis(dicarbonylrhodium).—*(*a*) *With methyl iodide.* μ-Etioporphyrinato-bis[dicarbonylrhodium(I)] (40 mg) [2] and di-μ-chloro-bis(dicarbonylrhodium) (18 mg) were dissolved in chloroform (1 ml) and methyl iodide (2 ml). An excess of anhydrous potassium carbonate was then added and the mixture set aside for 7 h at room temperature. Work-up in the usual way followed by preparative t.l.c. gave *methylrhodium*(III)*–etioporphyrin* (8 mg; 26%) and *acetylrhodium*(III)*–etioporphyrin* (9.5 mg; 29%).

(*b*) *With ethyl iodide.* A similar reaction using ethyl iodide (2 ml) for 48 h gave a mixture of *ethylrhodium*(III)*–etioporphyrin* (4 mg; 13%), *propionylrhodium*(III)*–etioporphyrin* (2.5 mg; 8%), and *rhodium*(III)*–etioporphyrin iodide* (11 mg; 31%).

Reaction of N-*Methylazaporphyrins with Di-μ-chloro-bis(dicarbonylrhodium).— Methylrhodium*(III)*–3,7,13,17-tetraethyl-2,8,12,18-tetramethyl-5-azaporphyrin* (12a). *N*-Methyl-3,7,13,17-tetraethyl-2,8,12,18-tetramethyl-4-azaporphyrin (70 mg; a 1 : 1 mixture of *N*-21 and *N*-23 isomers) [6] was dissolved in chloroform (50 ml) containing an excess of anhydrous sodium acetate, and di-μ-chloro-bis(dicarbonylrhodium) (100 mg) was added. The green solution turned red within 10 min and the *product* (30 mg; 35%) was isolated in the usual way and was identical with that described previously.[2]

Methylrhodium(III)*–2,3,7,8,12,18-hexamethyl-13,17-diethyl-5-azaporphyrin* (12b). Similarly, but more slowly, 2,3,7,8,12,18-hexamethyl-13,17-diethyl-5-azaporphyrin (52 mg) gave the corresponding methylrhodium(III)–azaporphyrin (37 mg; 58%) as red plates from chloroform–methanol, m.p. >300 °C, with slow decomposition from *ca.* 270 °C (Found: C, 63.15; H, 6.15; N, 12.95. $C_{30}H_{34}N_5Rh$ requires C, 63.48; H, 6.05; N, 12.34%); *m/e* 567 (M^+); τ 0.70 (s, 3 H, *meso*-H), 6.19 (q, 4 H, 2 CH_2Me), 6.56, 6.64, and 6.67 (all s, 3 × 6 H, Me), 8.32 (t, 6 H, 2 CH_2Me), and 17.19 (d, J_{Rh-H} 3.3 Hz, Rh–Me).

Dicarbonyl-(3,3′,4,4′,5-pentamethyldipyrromethenato)-rhodium(I) (15a).—3,3′,4,4′,5-Pentamethyldipyrromethene hydrobromide (352 mg) was dissolved in alcohol-free chloroform (300 ml). Anhydrous sodium acetate (10 g) was added to the solution followed by di-μ-chloro-bis(dicarbonylrhodium) (469 mg) and the mixture was stirred at room temperature for 15 min. Filtration of the mixture through a silica column and evaporation of the solvent under reduced pressure yielded a purple solid which was crystallised from methanol to give the product (390 mg; 88%) as purple needles, m.p. 141—144 °C (Found: C, 51.8; H, 4.75; N, 7.6. $C_{16}H_{17}N_2O_2Rh$ requires C, 51.62; H, 4.61; N, 7.52%); $\nu_{max.}$ 2 000 and 2 060 cm^{-1}; τ 2.75 (s, 1 H, pyrrole-H), 3.15 (s, 1 H, methene-H), 7.5 (s, 3 H, Me), 7.9 (s, 6 H, Me), 8.05 (s, 3 H, Me), and 8.1 (s, 3 H, Me).

Dicarbonyl-(3,3′,5,5′-tetraphenyldipyrroazamethenato)-rhodium(I) (15b).—3,3′,5,5′-Tetraphenyldipyrroazamethene (400 mg) [26] was dissolved in chloroform (100 ml). Anhydrous sodium acetate (1 g) was added to the solution followed by di-μ-chloro-bis[dicarbonylrhodium(I)] (430 mg). The mixture was stirred for 15 min and then filtered through a short silica column. The solvent was removed under reduced pressure to yield a blue solid which was crystallised from chloroform–methanol to give the product (510 mg; 94%) as dark blue needles, m.p. >300 °C (Found: C, 67.0; H, 3.50; N, 6.70. $C_{34}H_{22}N_3O_2Rh$ requires C, 67.22; H, 3.66; N, 6.92%); *m/e* 607 (M^+), 579 ([M − CO]$^+$, and 551 ([M − 2CO]$^+$); $\nu_{max.}$ 2 010 and 2 070 cm^{-1}; τ 2.0—2.7 (m, 20 H, phenyl) and 2.82 (d, 2 H, pyrrole-H).

Dicarbonyl-(2-phenylazo-3,5-dimethyl-4-ethoxycarbonylpyrrolato)rhodium(I) (16).—2-Phenylazo-3,5-dimethyl-4-ethoxycarbonylpyrrole (220 mg) was dissolved in chloroform (50 ml). Anhydrous sodium acetate (1 g) was added to the solution followed by di-μ-chlorobis[dicarbonylrhodium(I)] (200 mg) and the mixture stirred for 15 min at room temperature. The solution was then filtered through a short alumina column, and the solid obtained by evaporation of the filtrate was crystallised twice from methylene chloride to give the product (230 mg; 73%) as maroon needles, m.p. 166—168 °C (Found: C, 47.3; H, 3.65; N, 9.70. $C_{17}H_{16}N_3O_4Rh$ requires C, 47.56; H, 3.76; N, 9.79%); *m/e* 429 (M^+), 401 ([M − CO]$^+$), and 373 ([M − 2CO]$^+$); $\nu_{max.}$ 2 020 and 2 080 cm^{-1}; τ 2.4—2.74 (m, 5 H, Ph), 5.71 (q, 2 H, CH_2Me), 7.29 (s, 3 H, Me), 7.42 (s, 3 H, Me), and 8.63 (t, 3 H, CH_2Me).

μ-(1,19-*Dideoxy-2,3,7,13,17,18-hexamethyl-8,12-diethylbiladienato-a,c)bis[dicarbonylrhodium*(I) (17b).—1,19-Dideoxy-2,3,7,13,17,18-hexamethyl-8,12-diethylbiladiene-ac dihydrobromide (100 mg) was dissolved in chloroform (50 ml). Anhydrous sodium acetate (200 mg) was added to the solution followed by di-μ-chloro-bis[dicarbonylrhodium(I)] (50 mg). The mixture was stirred for 5 min and then filtered and the sodium acetate washed with chloroform (*ca.* 25 ml). Methanol (250 ml) was added to the maroon filtrate and the solvent evaporated under reduced pressure, keeping the temperature below 40 °C. When the volume of the solution was *ca.* 25 ml it was cooled in the refrigerator for 1 h. The solution was then filtered to give the product (15 mg; 12%), m.p. >300 °C (evolution of CO at *ca.*

260 °C) as brown plates which were washed well with methanol and dried (Found: C, 52.45; H, 4.55; N, 7.45. $C_{33}H_{34}N_4O_2Rh_2$ requires C, 52.39; H, 4.54; N, 7.41%); $\nu_{max.}$ 2 000 and 2 070 cm^{-1}; τ 2.72 (s, 2 H, pyrrole-H), 3.07 (s, 2 H, methene-H), 5.26 (s, 2 H, CH_2), 7.9 (m, 22 H, Me and CH_2Me), and 9.33 (t, 6 H, CH_2Me).

μ-(1,19-*Dideoxy*-1,3,7,13,17,19-*hexamethyl*-8,12-*diethylbiladienato-a,c*)-*bis*[*dicarbonylrhodium*(I)] (17a).—Prepared from 1,19-dideoxy-1,3,7,13,17,19-hexamethyl-8,12-diethylbiladiene-ac dihydrobromide (100 mg) in an analogous manner to the isomer above. The product (50 mg; 40%) formed light brown plates with a green reflex, m.p. >300 °C (slow decomposition from 155 °C, evolution of CO at *ca.* 260 °C) (Found: C, 52.4; H, 4.4; N, 7.4. $C_{33}H_{34}N_4O_2Rh$ requires C, 52.39; H, 4.54; N, 7.41%); $\nu_{max.}$ 2 000 and 2 070 cm^{-1}; τ 3.18 (s, 2 H, methene-H), 4.01 (s, 2 H, pyrrole-H), 5.44 (s, 2 H, CH_2), 7.62—7.91 (m, 22 H, Me and CH_2Me), and 9.25 (t, 6 H, CH_2Me).

Crystal Structure Determinations.—Cell parameters were first found from oscillation and Weissenberg photographs and then by least squares from the setting angles of 23 reflections on a Hilger–Watt four-circle diffractometer.

Crystal data. $C_{32}H_{35}N_4O_2Rh$, $M = 610.5$. Mo-K_α radiation (graphite monochromator), $\lambda = 0.710\,69$ Å. 21-Methyl compound: monoclinic, $a = 18.093(3)$, $b = 16.996(4)$, $c = 9.309(2)$ Å, $\beta = 90.31(3)°$, $U = 2\,862.6$ Å^3, $D_c = 1.417$ g cm^{-3}, $Z = 4$, $D_m = 1.42$ g cm^{-3}, $F(000) = 1\,264$. Space group $P2_1/n$ from systematic absences, $\mu = 6.20$ cm^{-1}. 22-Methyl compound: triclinic, $a = 8.899(2)$, $b = 11.929(3)$, $c = 14.449(3)$ Å, $\alpha = 101.39(2)$, $\beta = 104.37(2)$, $\gamma = 85.70(2)°$, $U = 1\,456.1$ Å^3, $D_c = 1.393$ g cm^{-3}, $Z = 2$, $D_m = 1.40$ g cm^{-3}, $F(000) = 632$. Space group $P\bar{1}$, $\mu = 6.09$ cm^{-1}.

Both crystals were scanned (ω–2θ mode) for $\theta \leqslant 25°$. The number of observed reflections (net count $\geqslant 3\sigma$) were 1 931 for the 21-methyl compound and 3 852 for the 22-methyl compound; Lorentz polarisation, but not absorption corrections, were applied. In each case the structures were solved routinely by the heavy-atom method and refined by least squares, ultimately with all non-hydrogen atoms treated anisotropically, in two blocks. Difference maps were calculated for both structures, and while the 21-methyl compound did not reveal convincing peaks attributable to hydrogen, that for the 22-methyl compound showed peaks corresponding to most of the expected hydrogen atoms. Accordingly, for this isomer only, hydrogens were included for the final cycles of refinement in positions in part taken from the difference map and in part calculated, but were not refined. The weighting schemes used were for the 21-methyl compound $W = \{1 + [(F_o - A)/B]^2\}^{-1}$, with $A = 11.0$ and $B = 14.0$, and for the 22-methyl isomer $W = [A(0)T(0)X + A(1)T(1)x + \ldots]^{-1}$ where the A values are the coefficients of a Chebyshev series in $T(i)x$ where $x = F_o/F_{max.}$; four terms were employed with $A(0) = -3.25$, $A(1) = 1.34$, $A(2) = -2.20$, and $A(3) = -1.89$.

The final R-values were; for the 21-methyl compound 6.4% and for the 22-methyl compound 4.4%. The relatively small number of observations for the 21-methyl case is reflected in the much larger standard deviations for the parameters for this molecule.

Table 1 contains the fractional co-ordinates for the 21-methyl compound, Table 2 those for the 22-methyl isomer. Tables 5 and 6 show respectively the bond lengths and bond angles for both isomers. Figures 1 and 2 are perspective drawings of the molecules,[27] while Figure 3 shows the crystallographic numbering. The drawings show the expected distortion of the *N*-substituted rings and this distortion is quantitatively described by the torsion angles The observed and calculated structure factors, anisotropic thermal parameters, and the torsion angles are deposited as Supplementary Publication No. SUP 22508 (77 pp.).* All computations were carried out using the Oxford ' CRYSTALS ' package.[28]

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* For details of Supplementary publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1977, Index issue.

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