# Structure and Reactions of Cobalt Corroles

By **Michael Conlon, Alan W. Johnson,** * **William R. Overend,** and **Dayananda Rajapaksa,** School of Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ
**Clive M. Elson,** A.R.C. Unit of Nitrogen Fixation, University of Sussex, Falmer, Brighton BN1 9QJ

Electrochemical studies on the cobalt corroles indicate that they are complexes of cobalt(III); these can exist as square planar, pyramidal, or octahedral complexes. Reaction of cobalt corrole with phenyl-lithium gives a phenyl derivative of cobalt(II) corrole where the additional phenyl group is probably attached to a nitrogen atom. Oxidation of triphenylphosphinecobalt(III) corroles with a high potential quinone causes conversion of the methyl groups at C-3 and C-17 into formyl substituents. Cobalt corroles may be obtained by a direct 2 + 2-type synthesis, and a related method has been used for the preparation of cobalt complexes of corrole itself.

SYNTHESES of tetrapyrrolic macrocycles, e.g. corroles [1] [e.g. (I)], 1-methyltetradehydrocorrins [2] [e.g. (II)], and 1,19-dialkyltetradehydrocorrin salts [3] [e.g. (III)], which contain a direct linkage between two of the pyrrolic rings, have involved the cyclisation of linear tetrapyrrolic derivatives, e.g. 1,19-dideoxybilenes-b, -biladienes-ac, or -bilatrienes and attempts at 2 + 2-type syntheses, e.g. condensation of α-unsubstituted 2,2'-bipyrroles with 5,5'-diformyl-2,2'-dipyrromethanes, have been unsuccessful. We now report that when a mixture of 3,3'-diethyl-4,4'-dimethyl-2,2'-bipyrrole-5,5'-dicarboxylic acid (IV; R = CO$_2$H) [4] and 3,3'-diethyl-5,5'-diformyl-4,4'-dimethyldipyrromethane (V; R = CHO) [1] in methanol was acidified at 0° with hydrobromic acid, a red precipitate was obtained which, when heated in methanol containing cobalt(II) acetate and triphenylphosphine, gave a cobalt 2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole containing an axial triphenylphosphine ligand. This is the first rational synthesis of one of these macrocyclic compounds by reactions which do

not involve the formation of the direct linkage as a final step.

The same product was obtained by the related condensation of 3,3'-diethyl-5,5'-diformyl-4,4'-dimethyl-2,2'-bipyrrole (IV; R = CHO) and 3,3'-diethyl-4,4'-dimethyl-2,2'-dipyrromethane-5,5'-dicarboxylic acid (V; R = CO$_2$H). These reactions presumably involve the intermediacy of a-norbilene-b intermediates (VI; R$^1$ = CHO, R$^2$ = CO$_2$H and R$^1$ = CO$_2$H, R$^2$ = CHO). Earlier attempts to cyclise such compounds in the absence of the complexing metal were unsuccessful, and the success of the cyclisations now reported stresses the importance of the cobalt, both for the stabilisation of the intermediate and in its template action in holding the reactive sites in proximity.

The stabilising effect of a co-ordinated triphenylphosphine ligand on cobalt corroles has been utilised in a synthesis of the triphenylphosphinecobalt(III) complex of corrole itself, i.e. containing no β-alkyl substituents.

[1] A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 1965, 1620.
[2] D. A. Clarke, R. Grigg, R. L. N. Harris, A. W. Johnson, I. T. Kay, and K. W. Shelton, *J. Chem. Soc.* (C), 1967, 1648.
[3] D. Dolphin, R. L. N. Harris, J. L. Huppatz, A. W. Johnson, and I. T. Kay, *J. Chem. Soc.* (C), 1966, 30.
[4] E. Bullock, R. Grigg, A. W. Johnson, and J. W. F. Wasley, *J. Chem. Soc.*, 1963, 2326.

Condensation of pyrrole with 5,5'-diformyl-2,2'-dipyrro-methane [5] gave 1,19-dideoxybiladiene-*ac* dihydrobro-mide in solution (stable for *ca.* 2 h) but the product decomposed on attempted isolation or on attempted cyclisations, either alone or in the presence of nickel,



(I)

(II)

(III)

(IV)

(V)

(VI)
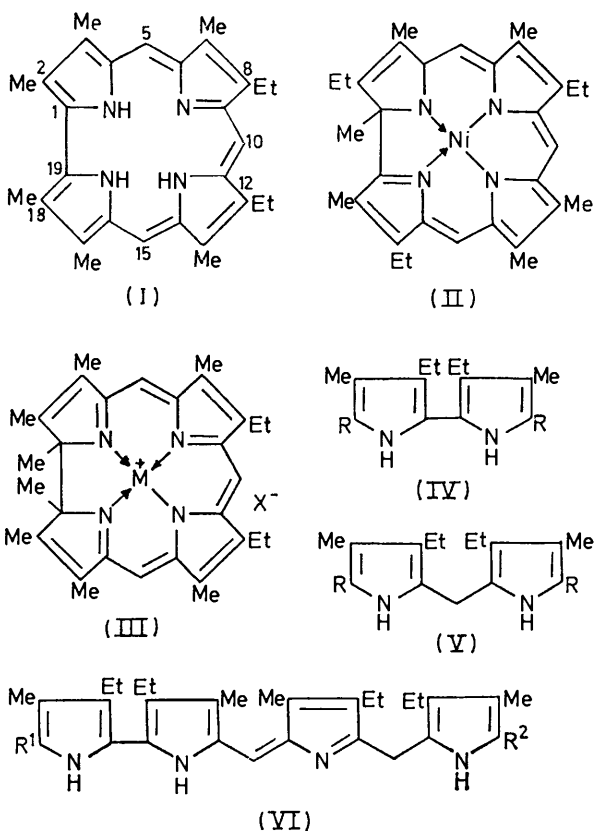
cobalt, or copper ions or with manganese(III) tris(acetyl-acetonate).[6] However, when the cyclisation was effected in the presence of cobalt(II) acetate and triphenylphos-phine, the triphenylphosphine derivative of cobalt(III) corrole was rapidly formed. The triphenyl phosphine ligand could be exchanged for pyridine.

Before the conditions for the successful cyclisation of 1,19-dideoxybiladiene-*ac* dihydrobromide were deter-mined, a number of related biladiene salts were prepared and in the cases of 2,18-dimethyl-, 1,19-diacetoxy-methyl-, and 1,2,18,19-tetrabromo-7,8,12,13-tetra-methyl-1,19-dideoxybiladiene-*ac* dihydrobromides, the conventional method of cyclisation was unsuccessful. Other cases were encountered where the normal method of condensation of 2-formylpyrroles, *e.g.* 5-bromo-,[7] 4,5-dibromo-,[7] and 5-ethoxycarbonyl-3,4-dimethyl-, with 2,2'-dipyrromethane did not yield the expected biladiene salt owing to deactivation of the formylpyrrole by the other substituents in the ring and the consequent longer exposure of the sensitive dipyrromethane to acid. For similar reasons, ethyl pyrrole-2-carboxylate and ethyl

3,4-dimethylpyrrole-2-carboxylate failed to react with 5,5'-diformyl-2,2'-dipyrromethane. All these inter-mediates were prepared for the possible development of improved routes to unsubstituted 1,19-dideoxybiladiene-*ac* dihydrobromide.

Corrole is a unique type of tetradentate macrocyclic ligand where three of the four nitrogen atoms carry replaceable hydrogen atoms. Cobalt corroles have been obtained previously by cyclisation of 1,19-dideoxy-biladienes-*ac* in hot methanol containing cobalt(II) acetate, as well as by the introduction of cobalt into the preformed corrole nucleus.[1] Two types of crystalline cobalt corrole were recognised; first, cobalt corroles con-taining no axial ligands which were thought to be com-plexes of cobalt(II) because of their paramagnetism, and secondly the products formed by addition of pyridine which were diamagnetic and regarded as octahedral dipyridinecobalt(III) complexes. Both these structures have now been shown to require modification. A re-examination of the pyridine derivative of cobalt(III) 2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole has indicated that the compound is a monopyridine derivative with no co-ordinated methanol or water (i.r. spectrum), and hence it is a pentaco-ordinate cobalt(III) corrole (VII; R = py). Similarly cyclisation of the 1,19-di-deoxybiladiene-*ac* dihydrobromide (VIII; R = H) in hot methanol containing cobalt(II) acetate and tri-phenylphosphine gave (VII; R = PPh₃; 2,18-Me₂ for 2,18-Et₂), a structure supported by n.m.r. and i.r. spectra. This product was identical with that obtained from the 2 + 2-type synthesis.



( VII )



( VIII )                                              2 Br⁻
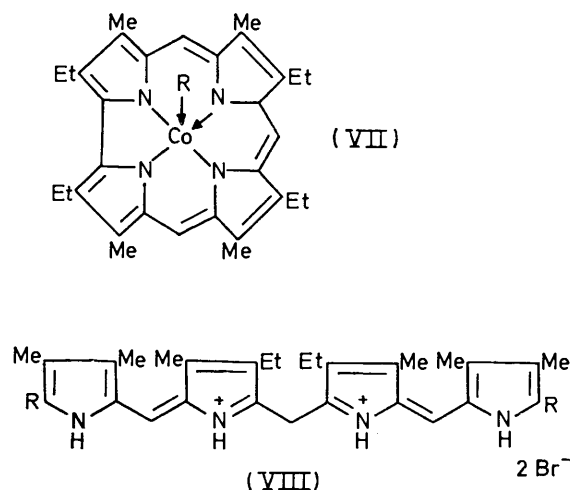
In contrast, when 8,12-diethyl-1,2,3,7,13,17,18,19-octamethyl-1,19-dideoxybiladiene-*ac* dihydrobromide (VIII; R = Me) was heated in methanol with cobalt(II) acetate and triphenylphosphine, a green paramagnetic product was precipitated within a few minutes. This was the dimeric form (IX) of the cobalt(II) complex of the biladiene;[3,8] this observation emphasises the

[5] A. W. Johnson and W. R. Overend, *J.C.S. Perkin I*, 1972, 2681.

[6] M. J. S. Dewar and T. Nakaya, *J. Amer. Chem. Soc.*, 1968, **90**, 7134.

[7] H. J. Anderson and S.-F. Lee, *Canad. J. Chem.*, 1965, **43**, 409.

[8] T. Murakami, Y. Kohno, and T. Matsuda, *Inorg. Chim. Acta*, 1971, **3**, 671.

hindrance to cyclisation caused by the terminal 1,19-methyl groups.



(IX)
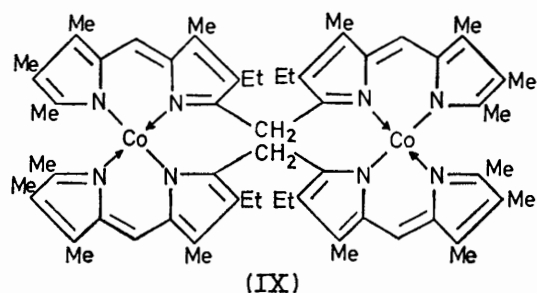
Although the majority of cobalt(III) complexes are octahedral a number of tetra- and penta-co-ordinate cobalt(III) derivatives are known,[9,10] including corrinoids,[11] and in one case [12] this has been confirmed by crystallography. In the mass spectra of the triphenylphosphine- and pyridine-cobalt(III) corroles, the axial ligand was readily eliminated and the ion of highest mass corresponded to the square planar cobalt complex (see later). A third type of penta-co-ordinate cobalt(III) corrole (VII; $R = p\text{-}CN\cdot C_6H_4\cdot CH_3$) was obtained from the corresponding pyridine derivative by reaction with $p$-tolyl isocyanide in chloroform.

When a chloroform solution of pyridine cobalt(III) corrole (VII; $R = $ py) was boiled, the pyridine was rapidly detached and a square planar cobalt corrole was obtained. This species was paramagnetic and was originally formulated as a cobalt(II) complex.[1] However, largely on the basis of results of controlled potential electrolyses (see later), these complexes are now regarded as paramagnetic square planar cobalt(III) derivatives (cf. refs. 13—15). The penta-co-ordinate triphenylphosphine and $p$-tolyl isocyanide complexes of cobalt(III) corrole were more stable than the pyridine analogue and were not decomposed even in boiling chlorobenzene. Addition of an excess of pyridine to solutions of either the square planar or the pyramidal cobalt corrole complexes markedly modified the electronic spectra, owing to the formation of the octahedral dipyridinecobalt(III) corrole which, however, was stable only in the presence of an excess of pyridine. Thus the cobalt corrole complexes as normally prepared are all derived from cobalt(III), i.e. all three of the corrole imine hydrogen atoms are replaced, and they exist as square planar, pyramidal, or octahedral complexes depending on the number of axial ligands. This is in sharp contrast to the behaviour of nickel,[16] palladium, and copper,[17] which yield corrole complexes derived from the divalent metal. However, when 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole was converted into its dianion and then treated with iron(II) chloride the crystalline paramagnetic iron(III) corrole complex was obtained.

Treatment of a solution of the square planar cobalt(III) corrole or any of the penta-co-ordinate derivatives in acetone with hydrobromic acid, gave a green crystalline paramagnetic hydrobromide, but the position of protonation has not yet been deduced. The protonation was reversible and addition of an excess of pyridine re-formed the pyridinecobalt(III) derivative.

Cobalt(III) porphins [18] and corrinoids [19] and cobalt(III) derivatives of other ligands [20,21] are known to react with Grignard reagents or with alkyl-lithiums to give octahedral alkyl- and aryl-cobalt(III) derivatives; treatment of a solution of square planar cobalt(III) corrole in tetrahydrofuran with phenyl-lithium or with phenylmagnesium bromide gave a green crystalline product (60%), the analytical figures of which ($C_{37}H_{40}CoN_4$) indicated the addition of one phenyl group to the cobalt corrole. The analogous $p$-tolyl derivative was also obtained but attempted alkylations of cobalt(III) corroles either with alkyl-lithiums or with alkylmagnesium bromides were unsuccessful. Alkylcobalt derivatives, e.g. of vitamin $B_{12}$ [22,23] and cobaloximes,[24] have also been obtained by chemical reduction of cobalt(III) to cobalt(I) and then treatment with alkyl halides. However, reduction of pyridinecobalt(III) corroles with sodium borohydride followed by treatment with methyl iodide again gave unstable green solutions which, after treatment with triphenylphosphine, gave the non-alkylated triphenylphosphinecobalt(III) corrole. The arylated cobalt corroles on the other hand were stable to light both as solids and in solution, and did not form penta-co-ordinate cobalt(III) corroles when they were warmed with pyridine or with triphenylphosphine. The aryl group was dissociated at ca. 130° and the resulting cobalt corrole was isolated as the triphenylphosphine complex. The arylated complexes were paramagnetic and non-polar, and are formulated as cobalt(II) corroles containing relatively labile aryl groups, which accords with the results of the electrochemical examination

[9] E. L. Muetterties and R. A. Schunn, Quart. Rev., 1966, 20, 245.

[10] G. Costa, G. Mestroni, L. Stefani, J. Organometallic Chem., 1966, 6, 181; 1967, 7, 493.

[11] H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, Chem. in Britain, 1969, 5, 156; J. M. Pratt and R. G. Thorp, Adv. Radiation Chem., 1969, 12, 402.

[12] S. Bruckner, M. Calligaris, G. Nardin, and L. Randaccio, Inorg. Chim. Acta, 1969, 3, 308.

[13] E. Billig, H. B. Gray, S. I. Shupack, J. H. Waters, and R. Williams, Proc. Chem. Soc., 1964, 110.

[14] M. Gerlock, B. M. Higson, and E. D. McKenzie, Chem. Comm., 1971, 1149.

[15] J. J. Bour, P. T. Beurskens, and J. J. Steggarda, J.C.S. Chem. Comm., 1972, 221.

[16] R. Grigg, A. W. Johnson, and G. Shelton, Annalen, 1971, 746, 32.

[17] R. Grigg, A. W. Johnson, and G. Shelton, J. Chem. Soc. (C), 1971, 2287.

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

[19] F. Wagner and K. Bernhauer, Ann. New York Acad. Sci., 1962, 112, 580.

[20] P. Day, H. A. O. Hill, and M. G. Price, J. Chem. Soc. (A), 1968, 90.

[21] G. Costa and G. Mestroni, Tetrahedron Letters, 1967, 4005.

[22] A. W. Johnson, L. Mervyn, N. Shaw, and E. Lester Smith, J. Chem. Soc., 1963, 4146.

[23] K. Bernhauer, O. Müller, and G. Müller, Biochem. Z., 1962, 336, 102.

[24] G. N. Schrauzer, A. Ribeiro, L. P. Lee, and R. K. Y. Ho, Angew. Chem. Internat. Edn., 1971, 10, 807.

(later). Moreover, in contrast to the behaviour of the cobalt(III) corroles, the arylated products were unaffected by addition of pyridine. The accumulated chemical evidence thus suggests that the aryl group is a substituent at N-21 (X; R = Ph), at N-22 (XI), or at cobalt (XII), but in the last case it will be evident that the ligand is the non-aromatic dehydro-corrole, a 16 π-electron system containing three cross-conjugated bonds which would not be expected, therefore, to show the aromatic type of visible spectrum observed for the product (*i.e.* containing a Soret band and small absorptions near 700 nm). The nickel(II), palladium(II), and copper(II) complexes of *N*-alkyl-corroles have been studied,[16,17] and in view of the failure to obtain the cobalt(II) analogues (see before), it is of interest that attempted introduction of cobalt(II) into the *N*(21)-methyl derivative of 8,12-diethyl-2,3,7,-13,17,18-hexamethylcorrole (X; R = Me; free base) resulted in the dissociation of the alkyl group and formation of the cobalt(III) derivative of the parent corrole.



(X)

(XI)

(XII)
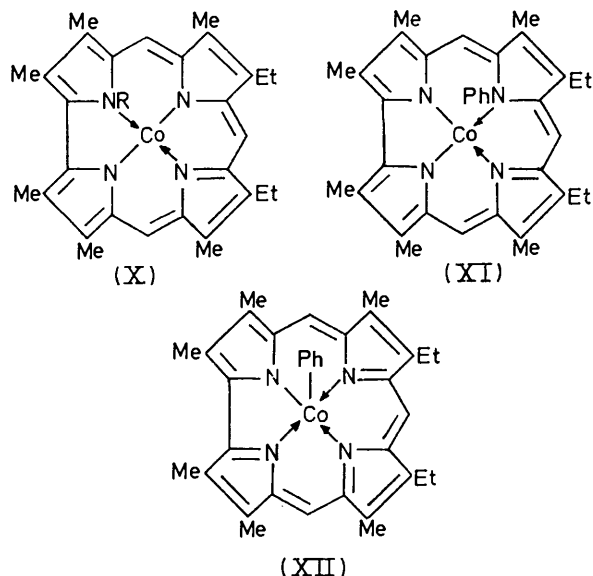
However, the final structure of the arylated cobalt corroles must await *X*-ray analysis and cannot be assigned on the chemical evidence available at present, although the spectral properties and the known chemical behaviour of *N*-alkylated corroles tend to favour the *N*(21)-phenyl formulation (X).

*Electrochemistry.*—The observed variation of the half-wave potential $(E_{\frac{1}{2}})$ with the nature of the axial ligand (Table) follows the expected pattern for the reduction of cobalt(III) to cobalt(II), *i.e.* increasing electron dona-tion by the axial ligand decreases the ease of reduction. However, the $E_{\frac{1}{2}}$ values for the oxidation of the cobalt-

(III) corroles only partially fit the predicted pattern. This is presumed to be the result of oxidation of the ligand, where the effect of the metal axial ligands would be diminished.

When pyridine was added to solutions of the square planar or pyramidal cobalt(III) complexes, but not the

Half-wave potentials of cobalt corroles in dichloro-methane–0·1M-tetraethylammonium chloride

| | $E_{\frac{1}{2}}/V$ [a,b] Reduction (+1e) | $E_{\frac{1}{2}}/V$ [c] Oxidation (−1e) |
|---|---|---|
| Square planar Co$^{III}$ corrole | −0·26 | +0·52 |
| + pyridine | −0·54 | +0·23 |
| Pyridine-Co$^{III}$ corrole | −0·35 | +0·25 |
| + pyridine | −0·54 | +0·17 |
| Triphenylphosphine-Co$^{III}$ corrole | −0·65 | +0·32 |
| + pyridine | −0·53 | +0·20 |
| *N*-Phenyl-C$^{II}$ corrole | −0·21 | +0·58 |
| + pyridine | −0·20 | |

[a] Relative to aqueous saturated potassium chloride–calomel electrode. [b] Measured by polarography at dropping mercury electrode. [c] Measured by cyclic voltammetry on platinum foil electrode at 90 mV s$^{-1}$.

phenylated product, the $E_{\frac{1}{2}}$ value (reduction) changed to −0·54 V in consequence of the formation of the octahedral dipyridine complex. A quantitative relation of the donor powers of axial ligands and half-wave potentials has been observed for the reduction of several series of cobalt(III) complexes.[25,26] The observed redox processes all involved one electron. With the exception of the reduction of the triphenylphosphine complex, all the reduction steps were reversible ($\alpha$ 1·0—0·85) as determined by 'log plot' analysis of the polarographic wave [27] and cyclic voltammetry.[28] On the other hand the oxidation of the corroles was quasi-reversible [29] (typically $\Delta E_p \simeq 200$ mV, $Ep_a - Ep_{a/2} \simeq 100$ mV).

A controlled potential reduction of the phenyl deriva-tive of cobalt 8,12-diethyl-2,3,7,13,17,18-hexamethyl-corrole gave a red solution which, in view of the lack of shift of chloroform and tetramethylsilane signals in the n.m.r. spectrum, was deduced to be diamagnetic. The aryl proton signals appeared as a multiplet at about τ 2·9. The reduced compound was very unstable and was readily oxidised to the original product by air. In contrast, a similar reaction of the square planar cobalt(III) corrole gave a paramagnetic species (shift of CHCl$_3$ and Me$_4$Si signals in n.m.r. spectrum).

By analogy with cobalt(III) porphins,[30] the electro-chemical oxidation step observed for cobalt(III) 2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole was assumed to be due to oxidation of the ligand but the products could not be isolated because of their instability. Chemical oxidation of triphenylphosphinecobalt(III) 2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole with an excess of DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone; *cf.* chlorins to porphins [31]) at room temperature gave as the

[25] G. Costa, G. Mestroni, A. Puxeddu, and E. Reisenhofer, *J. Chem. Soc. (A)*, 1970, 2870.
[26] G. Costa, A. Puxeddu, and G. Tauzher, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 319.
[27] L. Meites, 'Polarographic Techniques,' 2nd edn., Inter-science, New York, 1965, p. 214.

[28] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **36**, 706.
[29] R. S. Nicholson, *Analyt. Chem.*, 1965, **37**, 1351.
[30] G. Engelsma, A. Yamamoto, E. Markham, and M. Calvin, *J. Phys. Chem.*, 1962, **66**, 2517.
[31] U. Eisner and R. P. Linstead, *J. Chem. Soc.*, 1955, 3749.

major product (45%) a non-polar, diamagnetic, blue crystalline product. The n.m.r. spectrum suggested that the product was aromatic and symmetrical about the plane through C-10 and the cobalt atom. In addition the signals due to two of the four β-methyl groups were missing and instead there was an additional low-field resonance at $\tau$ $-0.80$ (two protons). Thus it appeared that the two methyl groups had been oxidised to formyl groups (cf. ref. 32), and the i.r. spectrum confirmed the presence of carbonyl groups. The elemental analysis indicated the formula $C_{49}H_{46}CoN_4O_2P$, i.e. the triphenylphosphine group was still present in the product although it was lost in the mass spectrometer, where the ion of highest $m/e$ value (530) corresponded to $C_{31}H_{31}CoN_4O_2$ ($M - PPh_3$). In order to decide which methyl groups had been oxidised, a similar oxidation of triphenylphosphinecobalt(III) 2,7,8,12,13,18-hexaethyl-3,17-dimethylcorrole was carried out, and a blue di-formyl compound was obtained in comparable yield (ca. 50%), i.e. it was the methyl groups at C-3 and C-17 which had undergone oxidation to give the diformyl derivative (XIII).

Although free isocyanides do not react with alcohols or amines, several co-ordinated isocyanides (XIV) undergo such additions to form metal–carbene complexes [e.g. (XV)].[33,34]



(XIII)   (XV)
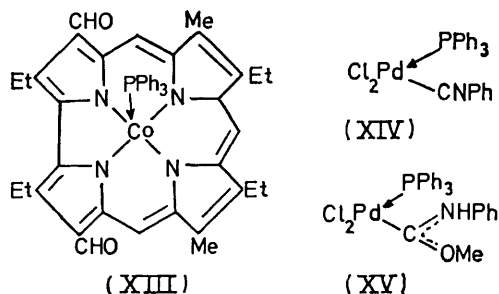
The possibility of modifying the axial ligand of (p-tolyl isocyanide)cobalt(III) 2,8,12,18-tetraethyl-3,7,13,17-tetra-methylcorrole (VII; $R = p\text{-}CN\cdot C_6H_4\cdot CH_3$) in a similar manner was investigated but the compound proved to be stable in boiling methanol, and no dissociation or modification of the axial ligand was observed. Treatment with a chloroform solution of p-toluidine caused replacement of the axial ligand as evidenced by the change in the visible spectrum and comparison with a sample prepared from the square planar cobalt(III) corrole and p-toluidine.

## EXPERIMENTAL

N.m.r. spectra were measured for deuteriochloroform solutions, i.r. spectra for Nujol mulls, and u.v.–visible spectra for chloroform solutions (except where otherwise stated) on the instruments listed in earlier papers in this series. Mass spectra were determined by direct sample insertion into the ion source of an A.E.I. MS9 instrument.

The electrochemical experiments employed the same apparatus as described previously.[35] M.p.s were determined on a Kofler hot-stage apparatus.

*Iron*(III) 8,12-*Diethyl*-2,3,7,13,17,18-*hexamethylcorrole*.— The parent corrole base was prepared following the method of Johnson and Kay[1] and showed $\tau$ 1·0 (s, 3 meso-H), 6·13 (q, $2 \times CH_2\cdot CH_3$), 6·57, 6·67, and 6·75 (all s, each $2 \times CH_3$), and 8·13 (t, $2 \times CH_2\cdot CH_3$); $\lambda_{max}$ (dry tetrahydrofuran containing a few drops of ethereal n-butyl-lithium) 418, 429, 550, and 584 nm ($\varepsilon$ 87,200, 65,000, 5700, and 4300).

An ethereal solution of phenyl-lithium (3%; 1 ml) was added with syringe to a solution of the corrole in dry tetra-hydrofuran under nitrogen. An excess of a suspension of anhydrous·iron(II) chloride in tetrahydrofuran was added to the resulting green solution of the corrole dianion. The mixture was stirred at room temperature for 10 min, poured into water, then extracted with dichloromethane ($2 \times 50$ ml). The combined extracts were washed with water, dried, and evaporated. The residue was then chromatographed on a column of alumina using chloro-form for elution. The first red band was collected; the eluate was evaporated and the residue crystallised from chloroform–methanol as deep red prisms (65 mg, 55%), m.p. >260° (decomp.) (Found: $M^+$, 491. $C_{29}H_{31}FeN_4$ requires $M$, 491·2) $\lambda_{max}$ 380 and 505 nm ($\varepsilon$ 75,600 and 14,200); $\lambda_{infl}$ 674 nm ($\varepsilon$ 2300). The mass spectrum contained no peak at $m/e$ 77, indicating the absence of an additional phenyl substituent.

*Cobalt*(III) 8,12-*Diethyl*-2,3,7,13,17,18-*hexamethylcorrole Hydrobromide*.—The corresponding pyridine derivative[1] was dissolved in hot acetone and methanolic 2N-hydro-bromic acid was added dropwise. The green solid which separated was filtered off and washed with methanol. Crystallisation from chloroform–methanol gave the *hydro-bromide* as green prisms (120 mg, 90%), m.p. >300° (Found: C, 59·9; H, 5·7; N, 9·45. $C_{29}H_{32}BrCoN_4$ requires C, 59·6; H, 5·5; N, 9·6%), $\lambda_{max}$ 356, 403, 422, and 650 nm ($\varepsilon$ 67,000, 25,200, 31,000, and 3700); $\lambda_{infl}$ 462 nm ($\varepsilon$ 5200). In an excess of pyridine, the salt re-formed the pyridine derivative.

*Pyridinecobalt*(III) 2,8,12,18-*Tetraethyl*-3,7,13,17-*tetra-methylcorrole*.—(a) 2,8,12,18-Tetraethyl-3,17,13,17-tetra-methylcorrole[16] (200 mg) and cobalt(II) acetate (200 mg) were dissolved in warm pyridine (10 ml) and heated at ca. 100° for 15 min. Boiling methanol (15 ml) was added and the mixture cooled to room temperature. The crystal-line solid was separated, washed with methanol (10 ml), and recrystallised from pyridine–light petroleum to give purple prisms (245 mg, 84%).

(b) Cobalt(II) acetate (200 mg) was dissolved in hot pyridine (10 ml), 2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-1,19-dideoxybiladiene-ac dihydrobromide[16] (250 mg) was added, and the mixture was heated on a steam-bath for ca. 10 min. Hot methanol (20 ml) was then added and the mixture was cooled to room temperature. The solid which separated was filtered off, washed with methanol (10 ml), and crystallised from pyridine–light petroleum to give purple prisms (210 mg, 86%) [Found: C, 71·3; H, 6·7; N, 11·5%; $m/e$, 522. $C_{36}H_{40}CoN_5$ requires C, 71·8; H, 6·65; N, 11·6%. $C_{31}H_{35}CoN_4$ ($M$ − pyridine) requires $m/e$,

[32] H. D. Becker, J. Org. Chem., 1965, **30**, 982.
[33] E. M. Bradley, J. Chatt, and R. L. Richards, J. Chem. Soc. (A), 1971, 21.

[34] B. Crociani and T. Boschi, J. Organometallic Chem., 1970, **24**, Cl.
[35] C. M. Elson, A. L. Hamilton, and A. W. Johnson, J.C.S Perkin I, 1973, 775.

522·5]; $\lambda_{max.}$ 383, 503, and 649 nm ($\varepsilon$ 105,000, 12,900, and 4100); $\lambda_{infl.}$ 724 nm ($\varepsilon$ 1700); $\lambda_{max.}$ (pyridine) 427, 502, 539, and 580 nm ($\varepsilon$ 85,300, 5250, 10,860, and 52,250); $\tau$ ($CS_2$) 0·42 (s, 2 meso-H at C-5 and C-15), 0·70 (s, meso-H at C-10), 3·10 and 4·78 (5H, both m, pyridine protons), 5·60 and 6·37 (both s, each 2 × $CH_3$), 6·16 and 6·22 (2 overlapping q, each 2 × $CH_2 \cdot CH_3$), and 8·00 (2 overlapping t, each 2 × $CH_2 \cdot CH_3$).

*Triphenylphosphinecobalt*(III)    2,8,12,18-*Tetraethyl-3,7,13,17-tetramethylcorrole.*— (a) 2,8,12,18-Tetraethyl-3,7,13,17-tetramethylcorrole (100 mg) was added to a solution of cobalt(II) acetate (100 mg) and triphenylphosphine (175 mg) in boiling methanol (20 ml). The solution was heated for ca. 10 min on a steam-bath, then cooled to room temperature. The purple crystalline solid was separated and recrystallised from dichloromethane–methanol to give reddish-purple prisms (148 mg, 82%).

(b) Pyridinecobalt(III) 2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole (100 mg) was heated with triphenylphosphine (175 mg) in boiling methanol for ca. 15 min, then the resulting deep red solution was cooled to room temperature. The product which separated was filtered off, washed with methanol (25 ml), and crystallised from dichloromethane–methanol to give reddish-purple prisms (98 mg, 76%).

(c) 2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-1,19-dideoxybiladiene-*ac* dihydrobromide (150 mg) was added to a solution of cobalt(II) acetate (200 mg) and triphenylphosphine (200 mg) in boiling methanol (100 ml). The mixture was heated until the initial precipitate redissolved (ca. 10 min) and the solution was cooled to room temperature. The solid was separated, washed with methanol, and crystallised from chloroform–methanol to give purple *prisms* (125 mg, 80%) [Found: C, 74·8; H, 6·6; N, 6·9% M (vapour phase osmometry), 767 ± 30; m/e, 522. $C_{49}H_{50}CoN_4P$ requires C, 75·0; H, 6·4; N, 7·1%; M, 784. $C_{31}H_{35}CoN_4$ ($M$ − $PPh_3$) requires m/e, 522·5]; $\lambda_{max.}$ 358 and 559 nm ($\varepsilon$ 56,500 and 18,800); $\lambda_{infl.}$ 378, 494, and 530 nm ($\varepsilon$ 48,400, 4350, and 7050); $\tau$ ($CS_2$) 0·54 (s, C-10 meso-H), 1·0 (s, C-5 and C-15 meso-H), 2·9—3·4 (9H, m, m- and p-protons of phenyl rings), 4·9—5·2 (6H, m, o-protons of phenyl rings), 6·25 and 6·33 (both q, each 2 × $CH_2 \cdot CH_3$), 6·63 and 6·77 (both s, each 2 × $CH_3$), and 8·26 and 8·29 (2 overlapping t, each 2 × $CH_2 \cdot CH_3$).

(d) 3,3'-Diethyl-4,4'-dimethyl-2,2'-bipyrrole-5,5'-dicarboxylic acid (100 mg) [4] and 3,3'-diethyl-5,5'-diformyl-4,4'-dimethyl-2,2'-dipyrromethane [1] (100 mg) were dissolved in methanol by warming the mixture to ca. 60°. The solution was then cooled in ice and aqueous hydrobromic acid (49%; 0·5 ml) was added dropwise with stirring. The red precipitate which formed was filtered off and washed with methanol (5 ml) containing a few drops of HBr. The solid was dissolved in hot methanol containing cobalt(II) acetate (200 mg) and triphenylphosphine (200 mg) and the solution was boiled on a steam-bath for 10 min before being cooled at 0° overnight. The solid which separated was filtered off, washed with methanol, and crystallised from chloroform–methanol to give purple prisms (54 mg, 21%).

(e) 3,3'-Diethyl-5,5'-diformyl-4,4'-dimethyl-2,2'-bipyrrole [36] (100 mg) and 3,3'-diethyl-4,4'-dimethyldipyrromethane-5,5'-dicarboxylic acid [1] (110 mg) were dissolved in methanol (20 ml). The solution was cooled in ice and aqueous hydrobromic acid (49%; 0·5 ml) was added dropwise with stirring. The red precipitate which formed was converted into the triphenylphosphinecobalt(III) complex

as in (d). The n.m.r. and visible spectra and t.l.c. behaviour of the product were identical with those of triphenylphosphinecobalt(III) 2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole (see before).

*Triphenylphosphinecobalt*(III)    2,3,7,8,12,13,17,18-*Octamethylcorrole.*—This was synthesised (70%) from 2,3,7,8,12,-13,17,18-octamethyl-1,19-dideoxybiladiene-*ac* dihydrobromide [1] by method (c) of the preceding section [Found: C, 74·9; H, 5·9; N, 7·6%; m/e, 466. $C_{45}H_{42}CoN_4P$ requires C, 74·9; H, 5·8; N, 7·7. $C_{27}H_{27}CoN_4$ ($M$ − $PPh_3$) requires m/e, 466·5]; $\lambda_{max.}$ 358 and 560 nm ($\varepsilon$ 57,200 and 20,100); $\lambda_{infl.}$ 378, 495, and 530 nm ($\varepsilon$ 48,000, 4300 and 7000); $\tau$ ($CS_2$) 0·70 (s, C-10 meso-H), 1·03 (s, meso-H at C-5 and C-15), 3·0—3·5 (9H, m, m- and p-protons of phenyl rings), 5·3 (6H, m, o-protons of phenyl rings), and 6·75—6·87 (24H, 4 overlapping s, each 2 × $CH_3$).

*Cobalt*(III)    2,7,8,12,13,18-*Hexaethyl-3,17-dimethylcorrole and Derivatives.*—The *triphenylphosphine derivative* was synthesised (65%) from 2,7,8,12,13,18-hexaethyl-3,17-di-methyl-1,19-dideoxybiladiene-*ac* dihydrobromide by method (c); the product was obtained as purple plates (Found: C, 75·2; H, 6·2; N, 7·1. $C_{51}H_{54}CoN_4P$ requires C, 75·4; H, 6·3; N, 6·9%); $\lambda_{max.}$ 358 and 559 nm ($\varepsilon$ 57,500 and 19,600); $\lambda_{infl.}$ 378, 494, and 530 nm ($\varepsilon$ 46,500, 4500, and 7500); $\tau$ ($CS_2$) 0·31 (s, meso-H at C-10), 0·58 (s, meso-H at C-5 and C-15), 2·7—3·3 (9H, m, m- and p-protons of phenyl rings), 5·2 (6H, m, o-protons of phenyl rings), 6·0, 6·1, and 6·2 (three overlapping q, each 2 × $CH_2 \cdot CH_3$), 6·33 (s, 2 × $CH_3$), and 7·8—8·0 (three overlapping t, each 2 × $CH_2 \cdot CH_3$).

The *pyridine derivative*, prepared (70%) from the foregoing 1,19-dideoxybiladiene dihydrobromide by method (b), showed $\lambda_{max.}$ 384, 503, and 649 nm ($\varepsilon$ 107,500, 12,400, and 4500); $\lambda_{infl.}$ 726 nm ($\varepsilon$ 1500); $\tau$ 0·71 (s, meso-H at C-5 and C-15), 0·85 (s, meso-H at C-10), 3·1 and 4·78 (both m, pyridine protons), 5·70 (s, 2 × $CH_3$), 5·9, 6·0, and 6·1 (all q, each 2 × $CH_2 \cdot CH_3$), and 8·02, 8·07, and 8·12 (all t, each 2 × $CH_2 \cdot CH_3$).

A solution of the pyridine compound (100 mg) in chloroform (20 ml) was boiled for 3 min. Hot methanol (20 ml) was added and the solution cooled to room temperature; *cobalt*(III), 2,7,8,12,13,18-hexaethyl-3,17-*dimethylcorrole* separated as brown hair-like needles (65 mg, 72%) which were separated, washed, and dried; m.p. >300° (Found: C, 71·45; H, 6·85; N, 9·95%; $M^+$, 551. $C_{33}H_{39}CoN_4$ requires C, 72·0; H, 7·15; N, 10·2%; M, 551); $\lambda_{max.}$ 385, 498, and 653 nm ($\varepsilon$ 102,000, 14,300, and 3200); $\lambda_{infl.}$ 473 nm ($\varepsilon$ 10,000). The n.m.r. spectrum ($CS_2$) was dependent on the concentration of the solution: (i) (40 mg in 1·0 ml of solvent), $\tau$ 4·75, 7·50, and 8·80 (all t, each 2 × $CH_2 \cdot CH_3$), 0·33 and 10·8 (both q, each 2 × $CH_2 \cdot CH_3$); (ii) (20 mg in 1·0 ml of solvent) $\tau$ 3·6, 7·2, and 8·9 (all t, each 2 × $CH_2 \cdot CH_3$) and 1·53—11·50 (both q, each 2 × $CH_2 \cdot CH_3$). The peripheral methyl groups, the three meso-protons, and the methylene protons of two ethyl groups could not be detected in the region $\tau$ −15 to +15 owing to broadening of the signals. When a drop of pyridine was added to the solution the spectrum sharpened and was identical with that detailed for the pyridine derivative.

*Cobalt*(III)    2,8,12,18-*Tetraethyl-3,7,13,17-tetramethyl-21-phenylcorrole.*—An excess of an ethereal solution of phenyl-lithium (2%; 2 ml) was added dropwise to a solution of pyridinecobalt(III)    2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole in dry tetrahydrofuran (50 ml) in an atmos-

[36] M. J. Broadhurst, R. Grigg, and A. W. Johnson, *J.C.S, Perkin I*, 1972, 2111.

phere of nitrogen. The colour of the solution changed from red to deep purple; the solution was stirred at room temperature for 10 min and then poured into water (100 ml). The green product was extracted into dichloromethane (2 × 50 ml) and the extracts were washed with water, dried, and evaporated. The residue was chromatographed on a column of alumina (chloroform for elution) and the first, green fraction afforded *cobalt*(II) *2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-21-phenycorrole*, which crystallised from dichloromethane as green needles (105 mg, 66%), m.p. >180° (decomp.) (Found: C, 74·45; H, 6·45; N, 9·2%; $M^+$, 600. $C_{37}H_{40}CoN_4$ requires C, 74·2; H, 6·7; N, 9·35%; $M$, 599·6); $\lambda_{max.}$ 374, 625, and 680 nm (ε 46,000, 2400, and 3750); $\lambda_{infl.}$ 422 (ε 7500); $\lambda_{max.}$ (CHCl₃ with 1 drop of CF₃·CO₂H) 347, 394, and 642 nm (ε 47,000, 8200, and 1450). When pyridine was added to the acidified solution the electronic spectrum of phenylated cobalt corroles was regenerated.

*Arylation of Cobalt*(III) *8,12-Diethyl-2,3,7,13,17,18-hexamethylcorrole.*—(i) Treatment of the pyridine derivative with *p*-tolyl-lithium by the foregoing procedure gave the N(21)-p-*tolyl derivative* (70%) as green prisms, m.p. >170° (decomp.) (Found: C, 74·2; H, 6·9; N, 9·1%; $M^+$, 585. $C_{38}H_{42}CoN_4$ requires C, 74·4; H, 6·5; N, 9·3%; $M$, 585·5); $\lambda_{max.}$ 376, 626, and 682 nm (ε 49,000, 2000, and 9200); $\lambda_{infl.}$ 425 nm (ε 8000).

(ii) A similar reaction with phenyl-lithium gave the N(21)-*phenyl derivative* (65%) (Found: C, 73·15; H, 6·3; N, 10·05%; $M^+$, 572. $C_{35}H_{36}CoN_4$ requires C, 73·5; H, 6·5; N, 9·8%; $M$, 572); $\lambda_{max.}$ 376, 625, and 681 nm (ε 47,500, 2500, and 4200).

*Thermolysis of Cobalt*(II) N(21)-*Arylcorroles.*—(i) 2,8,12,18-*Tetraethyl*-3,7,13,17-*tetramethyl*-21-*phenyl derivative.* The corrole (100 mg) was heated in refluxing, degassed, anhydrous chlorobenzene in an atmosphere of nitrogen for 2 h. The solvent was then evaporated off under reduced pressure and the residue was treated with triphenylphosphine (75 mg) in chloroform (5 ml). The chloroform solution was chromatographed on a column of neutral alumina (chloroform for elution). The first red band was collected; the eluate was evaporated to dryness, and the residue was crystallised from dichloromethane–light petroleum to give purple prisms (30 mg, 16%). The visible and n.m.r. spectra of the product were identical with those of triphenylphosphinecobalt(III) 2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole.

(ii) 8,12-*Diethyl*-2,3,7,13,17,18-*hexamethyl*-21-p-*tolyl derivative.* The corrole (100 mg) was heated in refluxing, degassed, dry toluene under nitrogen for 4 h; t.l.c. then indicated that no starting material was left. Triphenylphosphinecobalt(III) 8,12-diethyl-2,3,7,13,17,18-hexamethyl corrole (28 mg, 20%) was isolated as in (i).

*Oxidation of Triphenylphosphinecobalt*(III) *Corroles.*—(i) Triphenylphosphinecobalt(III) 2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole (100 mg) dissolved in chloroform (20 ml) was treated with a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (152 mg) in methanol (10 ml). The solution immediately turned deep blue and was stirred at room temperature for 2 h, after which no starting material remained (t.l.c.). The solvent was evaporated off under reduced pressure and the residue was extracted into dichloromethane. The mixture was filtered, the filtrate was evaporated, and the residue was purified by preparative t.l.c. (0·75 mm silica) [chloroform–light petroleum (9 : 1) as mobile phase]. The least polar, blue fraction was recovered and crystallised from dichloromethane–

methanol to give *triphenylphosphinecobalt*(III) *2,8,12,18-tetraethyl-3,17-diformyl-7,13-dimethylcorrole* as blue prisms (47 mg, 45%), m.p. >300° [Found: C, 72·7; H, 5·65; N, 7·3%, *m/e*, 550. $C_{49}H_{46}CoN_4O_2P$ requires C, 72·4; H, 5·7; N, 6·9%. $C_{31}H_{31}CoN_4O_2$ ($M$ — PPh₃) requires *m/e*, 550·6]; $\nu_{max.}$ 1645 cm⁻¹ (CHO); $\lambda_{max.}$ 370, 550, 592, and 633 nm (ε 27,000, 31,200, 14,000, and 25,200); $\lambda_{infl.}$ 465 nm (ε 18,650); τ −0·80 (s, 2 × CHO), 0·27 (s, *meso*-H at C-5 and C-15), 1·00 (s, *meso*-H at C-10), 3·0—3·6 (m, *m*- and *p*-protons of the three phenyl groups), 5·1—5·5 (m, *o*-protons of the three phenyl groups), 6·17 and 6·72 (both q, each 2 × CH₂·CH₃), 7·07 (s, 2 × CH₃), and 8·40 and 8·58 (two overlapping t, each 2 × CH₂·CH₃).

(ii) Triphenylphosphinecobalt(III) 2,7,8,12,13,18-hexaethyl-3,17-dimethylcorrole (100 mg) in chloroform–methanol was heated with an excess of DDQ at room temperature. The major, blue, non-polar fraction was separated as before and *triphenylphosphinecobalt*(III) *2,7,8,12,13,18-hexaethyl-3,17-diformylcorrole* was isolated as dark blue prisms (52 mg, 50%), m.p. >270° (decomp.) [Found: C, 72·4; H, 6·05; N, 6·85%; *m/e*, 578. $C_{51}H_{50}CoN_4O_2P$ requires C, 72·8; H, 6·0; N, 6·7%. $C_{33}H_{35}CoN_4O_2$ ($M$ — PPh₃) requires *m/e*, 578]; $\nu_{max.}$ 1645 cm⁻¹ (CHO); $\lambda_{max.}$ 371, 550, 593, and 635 nm (ε 28,200, 13,000, 14,300, and 26,000); $\lambda_{infl.}$ 465 nm (ε 19,000); τ −0·86 (s 2 × CHO), 0·12 (s, *meso*-H at C-5 and C-15), 1·00 (s, *meso*-H at C-10), 2·9—3·4 (m, *p*- and *m* protons of three phenyl groups), 5·0—5·3 (m, 2 *o*-protons of three phenyl groups), 6·1, 6·5, and 6·55 (all q, each 2 × CH₂·CH₃), and 8·26, 8·42, and 8·46 (3 overlapping t, each 2 × CH₃·CH₃).

(p-*Tolyl isocyanide*)*cobalt*(III) 2,8,12,18-*Tetraethyl*-3,7,13,17-*tetramethylcorrole.*—The corresponding pyridine complex (100 mg) in chloroform (20 ml) was mixed with *p*-tolyl isocyanide (0·2 ml) and the solution was stirred at room temperature for 0·5 h. Methanol (50 ml) was then added and the mixture was cooled (ice) for 2 h. The solid which separated was filtered off, washed with methanol, and crystallised from chloroform–methanol to give purple *plates* (89 mg, 85%), m.p. >280° (decomp.). The same product was obtained when cobalt(III) 2,8,12,18-tetraethyl-3,7,13,17-tetramethylcorrole was treated with *p*-tolyl isocyanide [Found: C, 74·7; H, 5·8; N, 9·9%; *m/e*, 522. $C_{39}H_{42}CoN_5$ requires C, 74·65; H, 6·2; N, 10·35%. $C_{31}H_{35}CoN_4$ ($M$ — PhNC) requires *m/e*, 522·6]; $\lambda_{max.}$ 510, 652, 680, and 712 nm (ε 68,900, 3500, 15,200, and 26,300); $\lambda_{infl.}$ 532 nm (ε 45,300); τ (CS₂) 0·65 (s, *meso*-H at C-10), 0·82 (s, *meso*-H at C-5 and C-15), 3·40 and 4·35 (both d, 4H of the benzene ring), 6·14 and 6·29 (2 overlapping q, 2 × CH₂·CH₃), 6·61, 6·70 (both s, each 2 × CH₃), 7·9 (s, *p*-tolyl CH₃), and 8·20 (two overlapping t, 2 × CH₂·CH₃).

*Triphenylphosphinecobalt*(III) *Corrole.*—2,2′-Dipyrromethane[5] (292 mg) and 2-formylpyrrole (380 mg) were dissolved in methanol (120 ml) and the solution was cooled to 0°. Hydrobromic acid (48%; 0·3 ml) was added and the mixture was stirred for 5 min and filtered. The solution of 1,19-dideoxybiladiene-*ac* dihydrobromide showed $\lambda_{max.}$ 435 and 500 nm. Triphenylphosphine (500 mg) and cobalt acetate (500 mg) were added to the filtrate and the mixture was shaken in dim light for 15 min. The precipitated solid was separated, washed with methanol, and crystallised twice from dichloromethane–light petroleum to give purple *prisms* (62 mg, 5%), m.p. >300° (Found: C, 71·8; H, 4·4; N, 9·55%; *m/e*, 354. $C_{37}H_{29}CoN_4P$ requires C, 71·7; H, 4·7; N, 9·05%. $M$ — Ph₃P requires *m/e*, 354); $\lambda_{max.}$ 291, 362, 391, 536, and 566 nm (ε 17,900, 48,100, 34,000, 8700,

and 10,200); $\lambda_{infl.}$ 512 nm ($\varepsilon$ 6700); $\lambda_{max.}$ (pyridine) 423, 434, 493, 524, 543, 567, and 589 nm ($\varepsilon$ 75,500, 68,400, 4500, 7650, 10,300, 34,200, and 34,800); $\lambda_{infl.}$ 404 nm ($\varepsilon$ 49,000) (see later); $\nu_{max.}$ 3050, 1570, 1540, 1515, 1485, 1435, 1400, 1310, 1280, 1090, 1055, 1040, 1030, 1010, 980, 855, 750, 705, and 530 cm$^{-1}$; $\tau$ 0·22 (s, 1 meso-H), 0·49 (s, 2 meso-H), 1·30—1·64 (m, 16β-H), 2·92—3·06 (m, 3H of phenyl groups), 3·27—3·44 (m, 6H of phenyl groups), and 5·31—5·50 (m, 6H of phenyl groups); $\tau$ ($C_5D_5N$) 0·19 (s, 2 meso-H), 0·41 (s, 1 meso-H), and 0·62—0·89 (m, 16β-H).

The triphenylphosphinecobalt(III) corrole (50 mg) was dissolved in pyridine (10 ml; redistilled) and the solution was stirred at room temperature for 10 min. On dropwise addition of methanol (20 ml), pyridinecobalt(III) corrole separated as purple prisms (29 mg, 85%), which were washed with methanol and dried (room temperature); m.p. $>300°$; $\lambda_{max.}$ 369, 515, 569, and 590 nm ($\varepsilon$ 61,100, 7350, 4320, and 3500); $\lambda_{infl.}$ 282 and 536 nm ($\varepsilon$ 13,300 and 6150) [the electronic spectrum of the product in pyridine solution was identical with that of triphenylphosphinecobalt(III) corrole in pyridine (see before)]; $\tau$ 0·10 (s, 2 meso-H), 0·21 (s, 1 meso-H), 0·91—1·21 (m, 16β-H), and 4·63—4·82 (m, 5H of pyridine).

*Preparation of Intermediates.*—1- *and* 2-*Ethoxycarbonyl-pyrroles.*—These were obtained (*cf.* ref. 37) by reaction of pyrrolylmagnesium bromide with ethyl chloroformate and separated by fractional distillation under reduced pressure. The 1-ethoxycarbonyl derivative (7·2%) was collected at 60—65° and 7 mmHg (Found: C, 60·95; H, 6·55; N, 10·5. Calc. for $C_7H_9NO_2$: C, 60·45; H, 6·45; N, 10·05%); $\lambda_{max.}$ 241 nm ($\varepsilon$ 6490), $\nu_{max.}$ 1750 cm$^{-1}$ (CO); $\tau$ 2·80 (m, 3-H and 4-H), 3·87 (m, 2-H and 5-H), 5·75 (q, $CH_2 \cdot CH_3$), and 8·73 (t, $CH_2 \cdot CH_3$). The 2-ethoxycarbonyl derivative (39·3%), m.p. 36—38°, was collected at 70—75° and 1 mmHg (Found: C, 60·4; H, 6·45; N, 10·05%); $\lambda_{max.}$ 264 nm ($\varepsilon$ 21,580); $\nu_{max.}$ 1685 (CO) and 3315 (NH); $\tau$ 3·05 (m, 4-H and 5-H), 3·77 (m, 3-H), 5·70 (q, $CH_2 \cdot CH_3$), and 8·72 (t, $CH_2 \cdot CH_3$). A further fraction, b.p. 93—98° at 1 mmHg, contained 1,2-bisethoxycarbonylpyrrole but this was not purified.

4-*Bromo-2-formyl-5-methylpyrrole.*—2-Formyl-5-methyl-pyrrole (100 mg) was dissolved in carbon tetrachloride and purified N-bromosuccinimide (163 mg) was added under nitrogen. The mixture was warmed at 50° for 2 h, cooled, and filtered into aqueous sodium carbonate (20%). The organic layer was separated and the aqueous layer extracted with ether. The combined organic extracts were dried and evaporated, and the residue was crystallised twice from light petroleum–ethyl acetate to give pale pink *crystals* (151 mg, 87%), m.p. 104—106° (Found: C, 38·45; H, 3·25; N, 7·25. $C_6H_6BrNO$ requires C, 38·3; H, 3·2; N, 7·45%); $\lambda_{max.}$ 253 and 307 nm ($\varepsilon$ 6450 and 17,190); $\nu_{max.}$ 1650 (CO) and 3240 (NH) cm$^{-1}$; $\tau$ 0·68 (s, CHO), 3·10 (d, 4-H), and 7·62 (s, $CH_2$).

5-*Acetoxymethyl-2-formylpyrrole.*—2-Formyl-5-methyl-pyrrole (2 g) was dissolved in glacial acetic acid (100 ml), lead tetra-acetate (8·06 g) was added, and the mixture was heated at 90—100° overnight under nitrogen. The solvent was removed under reduced pressure, water was added to the resulting oil, and the mixture was extracted with dichloromethane (5 × 25 ml). The extracts were dried, concentrated, and chromatographed on silica plates to give the *product* as the first major band. It was extracted into dichloromethane; the extract was dried and evaporated to yield a yellow oil which crystallised on cooling. Recrystallisation from light petroleum–ethyl acetate yielded plates (757 mg, 30%), m.p. 36—39° (Found: C, 58·5; H, 5·5; N, 8·1. $C_8H_9NO_3$ requires C, 58·9; H, 5·4; N, 8·4%); $\lambda_{max.}$ 250 and 290 nm ($\varepsilon$ 4900 and 19,970); $\nu_{max.}$ 1655 (formyl CO) and 1730 cm$^{-1}$ (acetate CO); $\tau$ 0·52 (s, CHO), 3·12 and 3·72 (both m, 3-H and 4-H, respectively), 4·87 (s, $CH_2$), and 7·95 (s, $CH_3$). A second band was unchanged starting material (691 mg, 35%).

2,3,17,18-*Tetrabromo*-1,7,8,12,13,19-*hexamethyl*-1,19-*dideoxybiladiene-ac dihydrobromide and* 2,3,17,18-*tetrabromo-*1,7,8,12,13,19-*hexamethyltetradehydrocorrin perchlorate.* 3,4-Dibromo-2-formyl-5-methylpyrrole (46 mg) and 3,3′,4,4′-tetramethyldipyrromethane-5,5′-dicarboxylic acid (25 mg) were dissolved in glacial acetic acid (20 ml) and aqueous hydrobromic acid (48%; 0·14 ml) was added. After 15 min at 20°, the precipitated salt was separated and washed with a little acetic acid and then with ether. The *dihydrobromide* was a dark red microcrystalline solid (47 mg, 64%), m.p. $>300°$, which decomposed on attempted crystallisation (Found: C, 35·5; H, 3·0; N, 6·4. $C_{25}H_{26}Br_6N_4$ requires C, 34·8; H, 3·0; N, 6·5%); $\lambda_{max.}$ 277, 378, 466, and 538 nm ($\varepsilon$ 60,900, 22,340, 41,630, and 141,100); $\lambda_{infl.}$ 504 nm ($\varepsilon$ 64,980); $\tau$ ($CF_3 \cdot CO_2H$) 2·87 (s, meso-5-H and 15-H), 5·92 (meso-10-$H_2$), 7·70 (s, $CH_3$ at C-1 and C-19), and 8·08 and 8·22 (both s, $CH_3$ at C-7, C-8, C-12, and C-13).

The dihydrobromide (500 mg) was dissolved in methanol (100 ml) and nickel acetate (500 mg) and sodium acetate (1 g) were added. The mixture was aerated, heated to boiling for 15 min, and then cooled to room temperature. The solution was filtered and sodium perchlorate (1 g) in water (500 ml) was added to the filtrate. The solution was then extracted with chloroform; the combined extracts were dried and concentrated until the *perchlorate* separated as purple crystals which were recrystallised from chloroform–light petroleum (yield 202 mg, 41%), m.p. $>300°$ (Found: C, 34·5; H, 2·5; N, 6·35. $C_{25}H_{21}Br_4ClN_4NiO_4$ requires C, 34·3; H, 2·5; N, 6·6%); $\lambda_{max.}$ 290, 364, and 580 nm ($\varepsilon$ 29,160, 24,490, and 12,210), $\lambda_{infl.}$ 470 nm ($\varepsilon$ 4430); $\tau$ ($CF_3 \cdot CO_2H$) 2·17 (s, 10-H), 2·28 (s, 5-H and 15-H), 7·47 (s, 4 × β-$CH_3$), and 8·97 (s, $CH_3$ at C-1 and C-19).

37 F. Signaigo and H. Adkins, *J. Amer. Chem. Soc.*, 1936, **58**, 1122; N. Maxim, I. Zugravescu, and I. Fulga, *Bull. Soc. chim. France*, 1938, **5**, 44.