Synthesis and Characterization of Novel Metal(III) Complexes of Corrole. Crystal and Molecular Structure of (2,3,7,8,12,13,17,18-Octamethylcorrolato)(triphenylarsine)rhodium(III) *

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Transition-metal complexes of 2,3,7,8,12,13,17,18-octamethylcorrole (H_3omc) have been prepared in high yield by means of three different synthetic procedures. The macrocycle acts as a trianionic ligand leading to the formation of neutral species. The crystal and molecular structure of the compound $[Rh(AsPh_3)(omc)]$ has been determined by *X*-ray diffraction methods. The crystals are orthorhombic, space group $P2_12_12_1$, with unit-cell dimensions $a = 20.172(7)$, $b = 12.468(5)$, $c = 14.893(5)$ Å, and $Z = 4$. The structure was solved by the heavy-atom technique and refined to $R = 0.0353$ for 1 436 independent reflections. The rhodium atom has a distorted square-pyramidal environment, the basal positions being occupied by the four nitrogen atoms from the corrole ligand and the apex by the arsenic atom from the triphenylarsine molecule.

Transition-metal complexes of tetrapyrrolic macrocycles have been widely studied for numerous reasons including their similarity to biologically important systems, their use as dyestuffs, and their applications in catalysis and photocatalysis.[1,2] Among the various macrocycles a very interesting one is corrole which can be considered as intermediate in structure between porphyrin and corrin (Figure 1): it has a direct link between the A and D pyrrole rings, thus resembling the corrin skeleton, and an 18-electron π system involving porphyrin-like conjugation, hence it is aromatic.[3]

Corrole bears obvious relation to corrin, the chromophore (as its cobalt complex) of vitamin B_{12} and its peculiar structure allows one to study the extent to which modifications of the porphyrin nucleus are possible while still retaining aromatic character and co-ordination ability towards metal ions.

The aromaticity of corrole is confirmed by its electronic spectrum which is characterized by two strong absorptions centred at about 400 and 600 nm. These bands have been attributed to π to π* transitions similar to the Soret and *Q* bands observed in the spectra of porphyrins. The lower symmetry of corrole is reflected by the fact that the higher-energy band is broader than the corresponding one for porphyrins so that it probably consists of two more unresolved transitions.[4]

Calculations of the π-electron distributions have been reported[5,6] indicating that a proton hole is located at N(22) and that the D ring is tilted out of the mean plane of the other three pyrrole rings. An *X*-ray study[7] performed on 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole has indeed shown that the molecule is not strictly planar, the distortion being probably caused by short N ⋯ N contacts brought about by the direct C(1)–C(19) link and by steric repulsion between the 2- and 18-methyl groups. Ring D is rotated by 8—10° but conjugation stabilization is still important since only small rotations of rings A—C are observed.

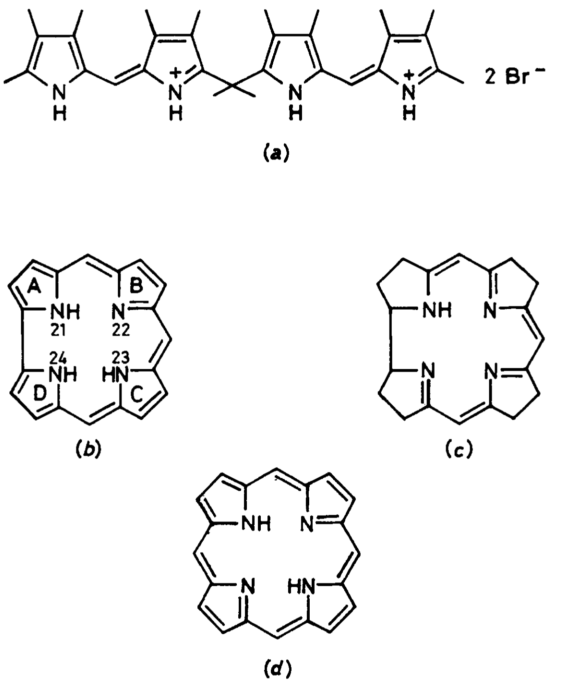

Figure 1. The structural formulae of 1,19-dideoxybiladiene-*ac* (*a*), corrole (*b*), corrin (*c*), and porphyrin (*d*)

The n.m.r. spectrum of corrole is a further proof of the existence of an aromatic system: all resonances show a strong upfield shift which has been attributed to the macrocycle ring current.[8]

As far as co-ordination with transition-metal ions is concerned, corrole having three amino-like nitrogens should act as a trianionic ligand stabilizing the metal(III) oxidation state with the formation of neutral complexes. Until 1988 however, the only example of a fully characterized metal(III) corrolate reported was a cobalt derivative.[4,9] The formation of metal(II) corrolates from the oxidative, base-induced cyclization of 1,19-

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Analytical data * for [M(omc)] complexes

M	Analysis (%) C	H	N
Cr	70.30	6.15	12.15
	(70.55)	(5.95)	(12.20)
Mn	69.90	6.00	12.30
	(70.10)	(5.90)	(12.10)
Fe	70.15	5.80	11.95
	(69.90)	(5.90)	(12.10)

* Required values are given in parentheses.

dideoxybiladiene-*ac* has also been reported (M = Ni, Cu,[3,10] or Pd[11]). The nickel and palladium complexes were non-aromatic with one of the potentially tautomeric hydrogen atoms displaced from nitrogen to carbon in such a way to interrupt the chromophore. Although the location of such a displaced proton has not yet been determined it has been arbitrarily placed at C(10). In contrast the electronic spectrum of the paramagnetic copper(II) complex is similar to those of the fully conjugated N(21)-methyl derivatives.[12,13]

In a previous paper[14] we reported on the synthesis of several rhodium corrolates. We have now extended the synthesis to first row transition metals and established three efficient and reproducible routes to metallocorrolates. Furthermore the *X*-ray crystal structure of (2,3,7,8,12,13,17,18-octamethylcorrolato)(triphenylarsine)rhodium(III) has been determined in order to ascertain the influence of co-ordination on the geometry of the macrocycle.

Experimental

I.r. spectra were recorded on a Perkin-Elmer model 983 spectrophotometer as Nujol mulls, electronic spectra on a Jasco model 7850 spectrophotometer. Dichlorotetracarbonyldirhodium was prepared following the procedure reported by McCleverty and Wilkinson.[15] Trirutheniumdodecacarbonyl was synthesized according to the literature procedure.[16] 1,19-Dideoxy-2,3,7,8,12,13,17,18-octamethylbiladiene-*ac* dihydrobromide (BD) as well as 2,3,7,8,12,13,17,18-octamethylcorrole (H_3omc) were prepared following the procedure previously reported.[14] All solvents (Farmitalia) were reagent grade and were used with no further purification.

Reactions of 1,19-*Dideoxy*-2,3,7,8,12,13,17,18-*octamethylbiladiene*-ac *Dihydrobromide with Metal Salts.*—The salts used were chromium(III) acetate, manganese-(II) or -(III) acetate, iron trichloride, and hydrated ruthenium trichloride. The biladiene (500 mg) and sodium acetate (1 g) were suspended in methanol (100 cm^3) and the stoicheiometric amount of the appropriate metal salt was added while stirring. The resulting green solution was refluxed for 3 (in the case of Fe and Ru) to 6 h (for Cr and Mn). Spectrophotometric analysis of the reaction mixture showed that when the reactions were carried out in the presence of chromium or ruthenium the product was the metal-free macrocycle. The solvent was then evaporated in a vacuum and the residue Soxhlet extracted with chloroform and purified by column chromatography on grade II acidic aluminium oxide (eluant: chloroform). Yields: 60—70%. When manganese or iron was used the product was the corresponding metal complex. The solvent was evaporated in a vacuum and the residue dissolved in tetrahydrofuran and chromatographed on grade II basic aluminium oxide [eluant: diethyl ether–tetrahydrofuran (1 : 1)]. Yields: 50—60%. Elemental analyses of metallocorrolates are reported in Table 1.

Reactions of Corrole.—With $Cr(O_2CMe)_3$, $Mn(O_2CMe)_3$, $FeCl_3$, *or* $RuCl_3$ *in dimethylformamide.* The corrole H_3omc (500 mg) was dissolved in dimethylformamide (dmf) (100 cm^3) together with the stoicheiometric amount of the appropriate metal salt and refluxed, under nitrogen, for 2 h. The solvent was evaporated in a vacuum and the residue chromatographed on Florisil (eluant: diethyl ether). Pure [M(omc)] (M = Mn or Fe) complexes were obtained by recrystallization from diethyl ether–n-hexane (1:2). In the presence of chromium salts extensive decomposition of the macrocycle was observed. When ruthenium was used the product was octamethylporphyrin.

With $[Cr(CO)_6]$, $[Mn_2(CO)_{10}]$, $[Fe(CO)_5]$, *or* $[Ru_3(CO)_{12}]$. The corrole H_3omc (500 mg) and the stoicheiometric amount of the appropriate metal carbonyl were dissolved in toluene (100 cm^3) and refluxed under a nitrogen atmosphere for 6 h. The solution was evaporated in a vacuum and the residues purified by recrystallization from diethyl ether–n-hexane (1:2). First-row transition metals yielded quantitatively the corresponding metal(III) corrolates. In the case of iron pentacarbonyl the addition of a catalytic amount of I_2 was necessary to activate the reaction.[17] When ruthenium was used the reaction products were octamethylporphyrin and its ruthenium(II) complex.

With $[\{Rh(CO)_2Cl\}_2]$. The corrole H_3omc (500 mg) and $[\{Rh(CO)_2Cl\}_2]$ (500 mg) were dissolved in benzene and refluxed for 6 h in the presence of triphenylarsine (500 mg). The solvent was evaporated in a vacuum and the residue chromatographed on grade II basic aluminium oxide [eluant: diethyl ether–tetrahydrofuran (1:1)]. The first fraction eluted was $[Rh(CO)_2(omc)]$[18] (yield: 10%) while the second was identified as $[Rh(AsPh_3)(omc)]$[14] (yield: 75%). Crystals of the latter suitable for *X*-ray crystallography were obtained by recrystallization from diethyl ether–n-hexane.

Crystallography.—Crystal data. $C_{45}H_{42}AsN_4Rh$, M = 816.68, a = 20.172(7), b = 12.468(5), c = 14.893(5) Å, U = 3 746(2) Å^3, Z = 4, D_c = 1.448 g cm^{-3}, Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 13.59 cm^{-1}, $F(000)$ = 1 672.

Data collection and reduction. A well formed crystal of dimensions 0.42 × 0.49 × 0.55 mm was mounted on a Siemens AED single-crystal computer-controlled diffractometer, which was employed to determine cell dimensions and to collect intensity data with the use of niobium-filtered Mo-K_α radiation. The crystal was found to be orthorhombic by peak-search, centring, and indexing procedures, and by reduced-cell calculations. Systematic extinctions in $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd uniquely determined the space group as $P2_12_12_1$. The unit-cell parameters and their estimated standard deviations were determined by a least-squares fit of diffractometer measured 2θ values for 29 intense reflections.

One octant of data was surveyed using a θ—2θ step-scanning technique with a scan speed ranging from 1.5 to 12° min^{-1}. In this way a total of 2 002 reflections (exclusive of systematic absences) was collected. Those 1 436 reflections for which $F_o > 4\sigma(F_o)$ were considered as observed and used for refinement. Due to the rather weak diffracting power of the crystal, data collection was terminated at $2\theta = 40°$ since only very few reflections were observed above this limit. No decrease in the intensity of a periodically remeasured reflection was noted. The intensities were processed with the peak-profile procedure following a local modification of the Lehman and Larsen method[19] and the data were corrected for Lorentz and polarization effects. Corrections for absorption and extinction effects were applied during the refinement according to the empirical method of Walker and Stuart.[20]

Structure analysis and refinement. The structure was solved by the heavy-atom technique. The position of the rhodium atom was found by using a three-dimensional Patterson map, which was calculated from the entire set of data, and all remaining non-

Table 2. Fractional atomic co-ordinates (× 10^5 for Rh and As, and × 10^4 for N and C)

Atom	X/a	Y/b	Z/c
Rh	233(5)	−16 478(8)	−5 120(7)
As	7 797(7)	−13 206(11)	6 210(10)
N(21)	−534(5)	−449(8)	−192(6)
N(22)	463(5)	−805(8)	−1 449(7)
N(23)	345(5)	−3 013(8)	−990(6)
N(24)	−636(5)	−2 354(9)	219(7)
C(1)	−1 050(6)	−613(11)	393(9)
C(2)	−1 358(6)	411(11)	510(10)
C(3)	−1 038(6)	1 150(11)	10(9)
C(4)	−492(6)	599(10)	−441(9)
C(5)	−39(8)	943(11)	−1 090(8)
C(6)	407(6)	293(11)	−1 559(8)
C(7)	866(7)	585(11)	−2 252(9)
C(8)	1 188(7)	−316(11)	−2 537(9)
C(9)	935(6)	−1 209(11)	−2 037(9)
C(10)	1 084(7)	−2 289(11)	−2 095(9)
C(11)	815(6)	−3 170(11)	−1 649(8)
C(12)	905(7)	−4 295(11)	−1 762(10)
C(13)	496(7)	−4 823(11)	−1 218(9)
C(14)	120(6)	−4 040(10)	−691(9)
C(15)	−375(7)	−4 189(13)	−55(10)
C(16)	−748(6)	−3 428(11)	367(8)
C(17)	−1 332(6)	−3 476(12)	928(8)
C(18)	−1 546(7)	−2 468(12)	1 097(10)
C(19)	−1 109(6)	−1 730(11)	620(10)
C(25)	−1 954(7)	662(13)	1 118(11)
C(26)	−1 192(9)	2 343(14)	−153(11)
C(27)	961(7)	1 733(12)	−2 618(10)
C(28)	1 717(7)	−374(13)	−3 263(10)
C(29)	1 376(7)	−4 793(12)	−2 434(10)
C(30)	402(7)	−5 990(11)	−1 101(10)
C(31)	−1 623(8)	−4 536(14)	1 220(12)
C(32)	−2 161(7)	−2 111(13)	1 603(11)
C(33)	1 484(4)	−2 368(7)	715(6)
C(34)	1 324(4)	−3 456(7)	690(6)
C(35)	1 822(4)	−4 226(7)	780(6)
C(36)	2 479(4)	−3 907(7)	895(6)
C(37)	2 639(4)	−2 819(7)	919(6)
C(38)	2 141(4)	−2 049(7)	829(6)
C(39)	366(4)	−1 294(8)	1 776(5)
C(40)	−72(4)	−462(8)	1 978(5)
C(41)	−409(4)	−457(8)	2 796(5)
C(42)	−308(4)	−1 284(8)	3 412(5)
C(43)	129(4)	−2 116(8)	3 210(5)
C(44)	466(4)	−2 121(8)	2 392(5)
C(45)	1 251(4)	25(6)	548(7)
C(46)	1 223(4)	772(6)	1 245(7)
C(47)	1 541(4)	1 760(6)	1 155(7)
C(48)	1 886(4)	2 001(6)	369(7)
C(49)	1 913(4)	1 254(6)	−327(7)
C(50)	1 596(4)	267(6)	−238(7)

Table 3. Selected bond distances (Å) and angles (°)

Rh–N(23)	1.956(10)	N(22)–C(6)	1.38(2)
Rh–N(22)	1.960(10)	C(6)–C(5)	1.40(2)
Rh–N(21)	1.930(10)	C(5)–C(4)	1.40(2)
Rh–N(24)	1.932(11)	C(4)–N(21)	1.36(2)
Rh–As	2.311(2)	N(21)–C(1)	1.37(2)
As–C(33)	1.934(9)	C(1)–C(19)	1.44(2)
As–C(39)	1.913(8)	C(19)–N(24)	1.37(2)
As–C(45)	1.931(8)	N(24)–C(16)	1.37(2)
N(23)–C(11)	1.38(2)	C(16)–C(15)	1.37(2)
C(11)–C(10)	1.39(2)	C(15)–C(14)	1.39(2)
C(10)–C(9)	1.38(2)	C(14)–N(23)	1.43(2)
C(9)–N(22)	1.39(2)		
N(23)–Rh–N(22)	93.3(4)	C(14)–C(15)–C(16)	128.1(14)
N(23)–Rh–N(21)	163.2(4)	C(15)–C(16)–N(24)	120.8(12)
N(23)–Rh–N(24)	92.1(4)	C(16)–N(24)–Rh	130.3(9)
N(22)–Rh–N(21)	91.4(4)	Rh–N(24)–C(19)	117.8(9)
N(22)–Rh–N(24)	163.3(4)	N(24)–C(19)–C(1)	113.0(11)
N(21)–Rh–N(24)	79.2(4)	C(19)–C(1)–N(21)	110.9(11)
N(23)–Rh–As	101.5(3)	C(1)–N(21)–Rh	118.9(9)
N(22)–Rh–As	97.3(3)	Rh–N(21)–C(4)	129.8(8)
N(21)–Rh–As	93.8(3)	N(21)–C(4)–C(5)	121.6(12)
N(24)–Rh–As	97.1(3)	C(4)–C(5)–C(6)	126.0(13)
Rh–As–C(33)	114.7(3)	C(5)–C(6)–N(22)	124.6(12)
Rh–As–C(39)	111.8(3)	C(6)–N(22)–Rh	125.3(8)
Rh–As–C(45)	115.9(3)	Rh–N(22)–C(9)	124.4(9)
C(33)–As–C(39)	105.5(4)	N(22)–C(9)–C(10)	122.9(12)
C(33)–As–C(45)	103.3(4)	C(9)–C(10)–C(11)	130.7(13)
C(39)–As–C(45)	104.5(4)	C(10)–C(11)–N(23)	119.7(12)
Rh–N(23)–C(14)	124.1(8)	C(11)–N(23)–Rh	127.7(8)
N(23)–C(14)–C(15)	124.1(12)		

hydrogen atoms were located through a combination of structure-factor calculations and Fourier difference syntheses. Full-matrix least-squares refinement was carried out minimizing $\Sigma w|\Delta F^2|$. Unit weights were used initially, while in the last stages of refinement a scheme of the form $w = 0.4016/[\sigma^2(F_o) + 0.001\ 479|F_o|^2]$ was applied. In order to reduce the number of variable parameters only the rhodium and arsenic atoms were allowed to vibrate anisotropically, and the three phenyl rings were refined as rigid groups of D_{6h} symmetry. The co-ordinates for the three methine hydrogen atoms were derived from a Fourier difference map and refined isotropically. All other hydrogens were added at idealized positions and included in the final structure-factor calculation. As the space group $P2_12_12_1$ is free of reflective elements, it was necessary to determine the absolute configuration of the crystal. Final refinement of the correct configuration resulted in R 0.0353, R' 0.0347, and R_g 0.0413. The corresponding values obtained by refinement of the enantiomorphic structure (for which all the signs of the co-ordinates were inverted) were 0.0440, 0.0435, and 0.0507, respectively. The ratio observations: variables was 6.6:1. The final Fourier difference map contained no peaks greater than 0.34 e Å^{-3}.

Complex atom scattering factors were employed, and corrections for anomalous dispersion were included for all non-hydrogen atoms.[21] Calculations were performed on a GOULD-SEL 32/77 computer using the program package SHELX 76[22] and other programs which have been cited elsewhere.[23]

Atomic co-ordinates for the non-hydrogen atoms are given in Table 2, selected bond distances and angles in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Two strategies can be considered to obtain metallocorrolates: (*a*) cyclization of the open-chain tetrapyrrolic precursor 1,19-dideoxybiladiene-*ac* in the presence of metal salts; (*b*) reactions of the preformed macrocycle with metal ions. The latter procedure can be performed either from metal salts and corrole in a co-ordinating solvent such as dmf or by using metal carbonyls in an inert organic solvent.

The reaction of 1,19-dideoxyoctamethylbiladiene-*ac* with transition-metal ions is strongly influenced by the nature of the metal. So with Mn and Fe the corresponding metallocorrolates

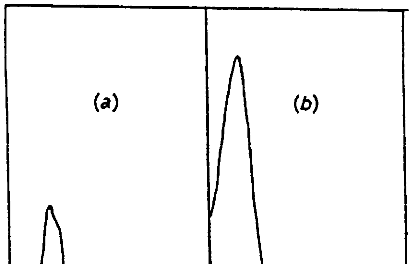

Figure 2. Absorption spectra of metallocorrolates in tetrahydrofuran: (*a*) [Rh(AsPh$_3$)(omc)], (*b*) [Fe(omc)], (*c*) [Mn(omc)], and (*d*) Cr(omc)]

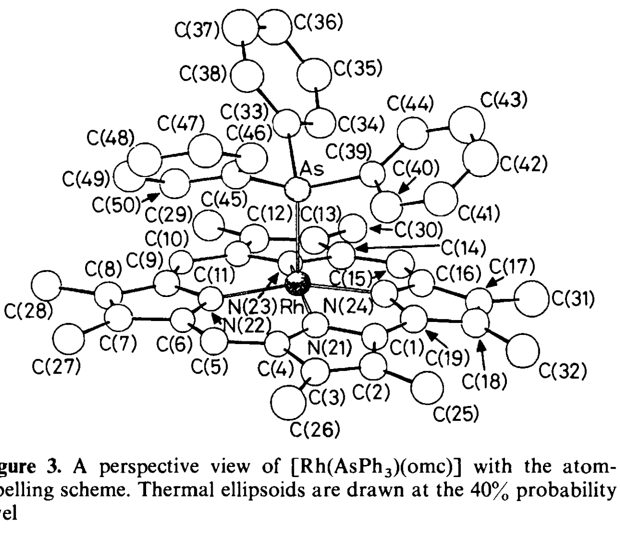

Figure 3. A perspective view of [Rh(AsPh$_3$)(omc)] with the atom-labelling scheme. Thermal ellipsoids are drawn at the 40% probability level

are obtained in high yield, in the presence of chromium or ruthenium the reaction product is the metal-free macrocycle, while co-ordination of rhodium requires the presence of an axial ligand such as a phosphine, arsine, or amine.[14]

The mechanism of this cyclization has been investigated in several studies.[2] It is catalysed by the presence of a base (sodium acetate has been used throughout this work) the first step being the formation of the green bilatriene free base. The solution goes from red to yellow with the formation of the biladiene monohydrobromide and then to green when the excess of base reacts to give the bilatriene. In the absence of metal ions cyclization can be achieved photochemically.[3]

Once the bilatriene is formed, co-ordination of a metal ion achieves the right geometry for cyclization. The metal stabilizes the intermediates and exerts a template action in holding the reactive sites in proximity. Since metal-free corrole is the product when chromium, ruthenium, or rhodium is used but no light is needed for the reaction to occur, we can assume that the metal participates in the cyclization process. The first product would be an unstable square-pyramidal out-of-plane complex, then the metal can collapse into the macrocycle plane with formation of the products.

The second synthetic method is the application to corroles of Adler's synthesis of metalloporphyrinates.[24] The solvent, dmf, is sufficiently basic to allow preparation only of manganese and iron corrolates. We have already reported[14] on the decomposition of the solvent and incorporation of dimethylamine into the resulting metal complex when rhodium trichloride is used in this procedure. Ruthenium decomposes the solvent as well, but the fragment utilized is carbon monoxide which is added to the macrocycle leading to the formation of octamethylporphyrin.

A final synthetic procedure which yields metallocorrolates is the reaction of metal carbonyls with corrole in a non-co-ordinating solvent. Again catalytically active ruthenium utilizes CO to give the corresponding porphyrin. The yield of the metallated porphyrin increases with reaction time: this is not surprising since the reaction of triruthenium dodecacarbonyl and porphyrin is a standard procedure for the synthesis of ruthenium porphyrinates.[25] The behaviour of rhodium carbonyl chloride with corrole resembles that observed with porphyrins:[26] the first product is a rhodium(I) complex which is then oxidized to a rhodium(III) derivative. However, in the formation of rhodium corrolates the presence of an axial ligand is essential to the stability of the complex.

All the metallocorrolates are aromatic, as shown by their electronic spectra (Figure 2) where an intense Soret-like band is present in the high-energy region. The spectra of all corrole complexes with first-row transition metals are very similar to those of the corresponding etio-type metalloporphyrinates. They can be classified as *d*-type hyper spectra, *i.e.* with extra bands apart from the *Q* and Soret ones in the visible region. In the case of porphyrins such bands have been attributed to ligand-to-metal charge-transfer transitions.[27]

The crystal structure of the compound [Rh(AsPh$_3$)(omc)] consists of discrete monomeric units where the rhodium atom may be regarded as exhibiting a distorted square-pyramidal co-ordination geometry with the basal plane defined by four nitrogen atoms from the corrole moiety and the apex of the pyramid occupied by the arsenic atom. A perspective view of the complex is given in Figure 3 with thermal ellipsoids enclosing 40% of the electron-probability distribution. The distortion from regular square-pyramidal geometry is mainly reflected in the two angles subtended at the metal by the diagonally opposite pairs of nitrogen atoms which are significantly narrower than 180° [N(21)–Rh–N(23) 163.2(4) and N(22)–Rh–N(24) 163.3(4)°]. Also distorted from the expected value of 90° is the N(21)–Rh–N(24) angle [79.2(4)°]. Other angles in the co-ordination sphere are all larger than 90° and fall in the range 91.4(4)—101.5(3)°. The above distortions are the result of the strain imposed on the whole complex by the geometric requirements of the corrole structure. Consistent with this, the four Rh–N bonds are not equivalent, with the two involving N(21) and N(24) not unexpectedly shorter than those involving N(22) and N(23). Furthermore N(21) ··· N(24) is 2.46(1) Å, compared with N(22) ··· N(23). 2.85(1), N(23) ··· N(24) 2.80(1), and N(21) ··· N(22) 2.78(1) Å. Somewhat longer

Rh^{III}–N bonds have been found for two other square-pyramidal rhodium porphyrin derivatives, *e.g.* 2.022(5)—2.041(6) Å in octaethylporphyrinato(methyl)rhodium[28] and 2.034(3)—2.037(3) Å in (octaethylporphyrinatorhodium)-octaethylporphyrinatoindium.[29]

The four co-ordinating nitrogen atoms are strictly coplanar, with the rhodium atom displaced by 0.26 Å from their plane towards the axial ligand. The angle formed by the Rh–As bond with the basal co-ordination plane is 86.1(2)°. The Rh–As bond distance of 2.311(2) Å is shorter than those found in the other four structurally characterized complexes with a Rh^{III}–As bond, all of which contain an octahedral metal environment. The four compounds and the corresponding distances are as follows: trichlorobis[(*o*-methoxyphenyl)dimethylarsine]rhodium, 2.333(5) and 2.354(6) Å;[30] *mer*-trichlorobis[(*o*-dimethylaminophenyl)dimethylarsine)rhodium, 2.342(4) Å for the chelating ligand and 2.529(5) Å for the unidentate ligand;[31] dichloro(η-methylallyl)bis(triphenylarsine)rhodium, 2.494(2) and 2.492(2) Å;[32] aquachloro-bis(trimethylarsine)tetrakis(trifluoromethyl)-rhodiacyclopentadiene, 2.436(2) Å.[33] This shortening is probably attributable to the lower co-ordination number of the rhodium atom in the present case. Of particular interest is the presence of a rather long, but directionally specific, intermolecular contact of 3.31(1) Å between the rhodium atom and one of the hydrogen atoms from the methyl carbon C(27) at $\bar{x}$, $y - \frac{1}{2}$, $\bar{z} - \frac{1}{2}$. This contact, which is located *trans* to the Rh–As bond, completes, a distorted octahedral co-ordination.

It is very interesting that the 15-atom core of the corrole moiety has an almost planar conformation, the largest deviation of atoms from the plane of best fit being 0.10 Å. The four pyrrole rings, which are strictly planar, are inclined 8—13° to each other and 2—10° to the square plane. The rhodium atom deviates up to 0.19 Å from the pyrrole mean planes and is displaced by 0.31 Å from the inner 15-membered ring.

Bond distances and angles in the pyrrole rings are in agreement with expected values, the average N–C$_\alpha$, C$_\alpha$–C$_\beta$, C$_\beta$–C$_{\beta'}$, and C$_\alpha$–N–C$_\alpha$ being respectively 1.38, 1.44, 1.35 Å, and 110°.

As a consequence of the corrole co-ordination, three RhNCCCN and one RhNCCN chelation rings are formed. The atoms of the five-membered ring are close to being coplanar, with no atom deviating by more than 0.04 Å from the least-squares plane, whereas those of the six-membered rings deviate slightly, but significantly, from coplanarity (maximum deviation 0.10 Å). In all of these rings the nitrogen and the carbon atoms are on opposite sides of the plane of best fit with the rhodium atom lying exactly on it.

As indicated by a search of the Cambridge Crystallographic Database, only four examples of structures of metallocorroles are presently known, namely (8,12-diethyl-2,3,7,13,17,18,21-heptamethylcorrolato)copper(II),[34] corrolato(triphenylphosphine)-cobalt(III),[35] dicarbonyl(8,12-diethyl-2,3,7,13,17,18,21-heptamethylcorrolato)rhodium(I), and dicarbonyl(8,12-diethyl-2,3,7,13,17,18,22-heptamethylcorrolato)rhodium(I).[18] The striking and distinctive feature of the latter two compounds is their out-of-plane nature. Of the four pyrrole rings, only two, *cis* to each other, are involved in bonding to the metal and one of the remaining rings is N-methylated. Such a ring is also present in the in-plane copper complex, where it is distorted considerably out of the plane of the rest of the molecule. The best example for comparison is therefore the cobalt complex, but, despite the similarity in the metal environment (with a Co $\cdots$ H contact of 3.0 Å filling the vacant sixth co-ordination site of the metal) and in the ligand behaviour, detailed discussion of the geometry of the corrole moiety is precluded by an approximately two-fold disorder.

The arsenic atom has a distorted tetrahedral environment with the Rh–As–C angles all larger than 109.5° and the C–As–C angles all smaller than 109.5°. The three phenyl rings differ slightly in orientation with respect to the plane defined by the three carbon atoms bonded to arsenic [47.7(3) for C(33)—C(38), 29.5(3) for C(39)—C(44), and 40.6(3)° for C(45)—C(50)]. The As atom deviates up to 0.11 Å from the plane of each ring. The As–C distances and the As–C–C angles have normal values, and average 1.926 Å and 120.0° respectively.

The molecular packing indicates only normal van der Waals forces between the molecules; the closest non-hydrogen contact distance, 3.37(2) Å, occurs between N(23) and C(27) at $\bar{x}$, $y - \frac{1}{2}$, $\bar{z} - \frac{1}{2}$.

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