

Fig. 1. Molecular structure and atom-numbering scheme. Thermal ellipsoids drawn at 30% probability level.

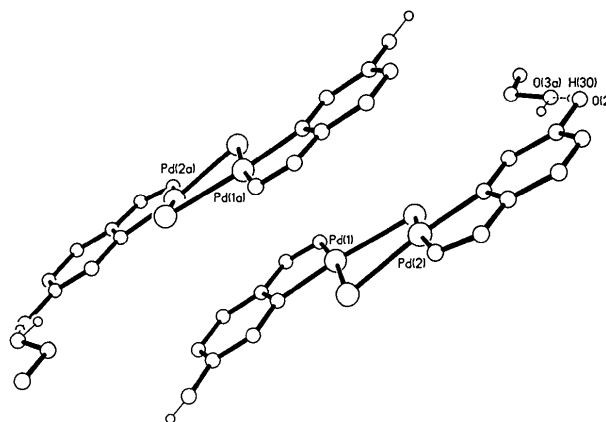


Fig. 2. A molecular dimer viewed along the *c* crystallographic axis ('free' phenyl rings removed for clarity).

dimethylbenzylamines (Barr, Dyke, Smith, Kennard & McKee, 1985).

The phenyl rings *A* and *B* are planar and tilted by 34.6 (2) and 47.4 (2)° with respect to the Pd(1) and Pd(2) mean coordination planes, respectively. The H(12)---Cl(1) and H(14)---Cl(2) distances are normal.

The crystal packing (Fig. 2) is characterized by discrete pairs of dimers which show weak intermolecular association. The shortest metal-metal contact [Pd(1)—Pd(1a); $-x, -y, -z + 1$], 3.620 (1) Å is greater than 3.2 Å, the van der Waals radii sum (Pauling, 1960). There is a hydrogen bond with a solvate molecule [O(2)---O(3a); $-x + 1, -y + 1, -z + 1$] = 2.60 (1), O(2)—H(30) = 0.91 (1) Å; O(2)—H(30)—O(3a) = 173 (1)°].

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Structure of a New Form of Octaethylporphyrinato(methyl)rhodium(III)

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Abstract. C₃₇H₄₇N₄Rh, *M_r* = 650.72, triclinic, *P* $\bar{1}$, *a* = 10.973 (1), *b* = 11.875 (1), *c* = 14.211 (1) Å, α =

108.03 (1), β = 105.41 (1), γ = 100.92 (1)°, *V* = 1616.0 (7) Å³, *Z* = 2, *D_x* = 1.337 g cm⁻³, $\lambda(\text{Mo K}\alpha_1)$ = 0.7093 Å, μ = 5.5 cm⁻¹, *F*(000) = 684, *T* = 295 K, final *R* = 0.044 for 4775 reflections [*F_o* > 3σ(*F_o*)]. The

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present structure is different from the one reported earlier [Takenaka, Syal, Sasada, Omura, Ogoshi & Yoshida (1976). *Acta Cryst.* **B32**, 62–65]: the Rh—C distance is somewhat shorter [1.970 (4) Å]; all the ethyl groups, except for a disordered one, are oriented toward the methyl group attached to Rh; the two nearest neighbors form a 'dimer' in which the Rh—Rh distance is 4.67 Å and the mean plane separation is 3.35 Å.

Introduction. The rhodium–carbon bond is one of the strongest metal–carbon bonds (Farnos, Woods & Wayland, 1986). We are interested in the effect of axial ligands on Rh—C bond distances in a series of rhodium porphyrin complexes, Rh(porphyrin)-(CH₃)(L) where L is an axial ligand. In an attempt to prepare octaethylporphyrinato(methyl)(1-methylimidazole)rhodium we accidentally obtained crystals of Rh(oep)(CH₃) (where oep = octaethylporphyrinato) whose structure turned out to be different from the one reported earlier (Takenaka, Syal, Sasada, Omura, Ogoshi & Yoshida, 1976).

Experimental. Crystals of the title compound were formed when *n*-hexane was allowed to diffuse into a solution of Rh(oep)(CH₃) (Ogoshi, Omura & Yoshida, 1973) in CH₂Cl₂ containing 1-methylimidazole (*ca* 10%). Dark red crystal, 0.35 × 0.50 × 0.17 mm; Enraf–Nonius CAD-4 diffractometer; monochromated Mo K α radiation; 25 reflections (11 < θ < 15°) used for measuring lattice parameters; $\omega/2\theta$ scan, ω -scan width of (0.80 + 0.34tan θ)°; max. sin θ/λ = 0.5958 Å⁻¹; -12 ≤ h ≤ 12, -14 ≤ k ≤ 13, 0 ≤ l ≤ 16; 5865 reflections measured, averaged to 5367 unique data (agreement: 1.6% on I , 1.3% on F), 4775 observed [$I > 3\sigma(I)$]. The intensities of four standard reflections (2 $\bar{1}$ 4, 2 $\bar{3}$ 2, 4 $\bar{7}$ 1, 0 $\bar{3}$ 2), recorded after every 3 h of X-ray exposure, decayed by 11.4% on average by the end of the data collection. The data were corrected for crystal decay, Lorentz–polarization and absorption effect; empirical absorption correction (relative transmission factor: 0.897–1.000) based on azimuthal (ψ) scans of six reflections. Structure solved by Patterson and Fourier synthesis methods. One of the ethyl groups was disordered; its methyl C atom was disordered over two sites (C28 and C28') which were subsequently shown (by refinement) to have 0.52 and 0.48 occupancies, respectively; however, attempts to resolve its methylene carbon (C27) into two different sites failed (see Fig. 1). Full-matrix least-squares refinement on F ; function minimized, $\sum w(|F_o| - |F_c|)^2$, $w = 4F_o^2/\sigma^2(I)$ with $\sigma(I) = [\sigma(I)^2 + (pF_o^2)^2]^{1/2}$ ($p = 0.04$), all non-H atoms refined anisotropically; H atoms attached to C37 atom found from difference Fourier map; the other H atoms positioned according to idealized geometry (C—H =

Table 1. Fractional coordinates and equivalent isotropic thermal parameters for non-H atoms with *e.s.d.*'s in parentheses

$$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}a_i\cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Rh	-0.20009 (3)	0.03034 (3)	0.01373 (3)	2.701 (7)
N1	-0.2849 (3)	0.1189 (3)	-0.0763 (2)	2.91 (8)
N2	-0.2112 (3)	0.1537 (3)	0.1438 (2)	3.01 (9)
N3	-0.1110 (3)	-0.0544 (3)	0.1044 (2)	2.94 (8)
N4	-0.1857 (3)	-0.0897 (3)	-0.1155 (2)	2.81 (8)
C1	-0.3183 (4)	0.0831 (3)	-0.1822 (3)	3.3 (1)
C2	-0.3812 (4)	0.1685 (3)	-0.2170 (3)	4.0 (1)
C3	-0.3837 (4)	0.2526 (3)	-0.1295 (3)	3.6 (1)
C4	-0.3242 (4)	0.2235 (3)	-0.0402 (3)	2.9 (1)
C5	-0.3108 (4)	0.2848 (3)	0.0630 (3)	3.1 (1)
C6	-0.2609 (4)	0.2546 (3)	0.1480 (3)	3.2 (1)
C7	-0.2566 (4)	0.3164 (4)	0.2537 (3)	4.2 (1)
C8	-0.2059 (4)	0.2547 (4)	0.3147 (3)	4.6 (1)
C9	-0.1775 (4)	0.1538 (4)	0.2422 (3)	3.7 (1)
C10	-0.1204 (4)	0.0688 (4)	0.2730 (3)	4.1 (1)
C11	-0.0903 (4)	-0.0270 (3)	0.2080 (3)	3.4 (1)
C12	-0.0294 (4)	-0.1139 (3)	0.2420 (3)	3.7 (1)
C13	-0.0175 (4)	-0.1928 (3)	0.1562 (3)	3.4 (1)
C14	-0.0688 (4)	-0.1564 (3)	0.0693 (3)	3.1 (1)
C15	-0.0766 (4)	-0.2152 (3)	-0.0330 (3)	3.3 (1)
C16	-0.1319 (4)	-0.1874 (3)	-0.1197 (3)	3.1 (1)
C17	-0.1471 (4)	-0.2567 (3)	-0.2267 (3)	3.6 (1)
C18	-0.2090 (4)	-0.2015 (3)	-0.2881 (3)	3.7 (1)
C19	-0.2330 (4)	-0.0985 (3)	-0.2160 (3)	3.3 (1)
C20	-0.2953 (4)	-0.0175 (3)	-0.2477 (3)	3.8 (1)
C21	-0.4261 (5)	0.1622 (4)	-0.3280 (4)	6.6 (2)
C22	-0.5595 (6)	0.0790 (6)	-0.3852 (5)	10.4 (2)
C23	-0.4403 (4)	0.3630 (4)	-0.1217 (4)	4.7 (1)
C24	-0.5799 (4)	0.3334 (4)	-0.1176 (4)	6.3 (2)
C25	-0.3024 (4)	0.4322 (4)	0.2883 (4)	5.6 (1)
C26	-0.4509 (5)	0.3982 (5)	0.2596 (4)	7.5 (2)
C27	-0.1808 (5)	0.2841 (4)	0.4295 (4)	6.6 (2)
C28'	-0.0699 (9)	0.3653 (9)	0.5012 (7)	5.0 (3)
C28	-0.262 (1)	0.229 (1)	0.4527 (7)	8.4 (4)
C29	0.0114 (5)	-0.1106 (4)	0.3522 (4)	5.3 (1)
C30	-0.0983 (6)	-0.1813 (5)	0.3763 (4)	8.5 (2)
C31	0.0360 (4)	-0.3032 (3)	0.1466 (4)	4.2 (1)
C32	-0.0748 (5)	-0.4245 (4)	0.1050 (4)	5.7 (2)
C33	-0.1044 (4)	-0.3728 (4)	-0.2625 (3)	4.5 (1)
C34	-0.2098 (5)	-0.4886 (4)	-0.2781 (4)	6.0 (2)
C35	-0.2451 (5)	-0.2365 (4)	-0.4052 (3)	5.2 (1)
C36	-0.3827 (6)	-0.3181 (5)	-0.4675 (4)	7.9 (2)
C37	-0.3735 (4)	-0.0819 (4)	-0.0120 (3)	4.5 (1)

0.95 Å) and given isotropic B 's of 1.2 times B of attached atom (H atoms attached to disordered ethyl group not included); final cycle of refinement on F including 389 variables converged to $R = 0.045$, $wR = 0.033$, $S = 3.23$; final $(\Delta/\sigma)_{\max} = 0.21$; the highest and lowest peaks in the final difference map were 1.23 (near Rh atom) and $-0.95 e \text{ \AA}^{-3}$, respectively; atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV) for the non-H atoms and from Stewart, Davidson & Simpson (1965) for H; all the calculations were carried out with the Enraf–Nonius (1980) *Structure Determination Package*. Table 1* gives atomic coordinates and equivalent isotropic thermal parameters of the non-H atoms

* Lists of structure factors, anisotropic thermal parameters, bond distances and angles for all non-H atoms, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54428 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected bond distances (Å) and angles (°)

Rh—N1	2.043 (3)	C11—C12	1.463 (6)
Rh—N2	2.021 (3)	C13—C14	1.442 (6)
Rh—N3	2.032 (3)	C16—C17	1.434 (6)
Rh—N4	2.012 (3)	C18—C19	1.450 (6)
Rh—C37	1.970 (4)	C2—C3	1.342 (6)
N1—C1	1.353 (5)	C7—C8	1.374 (7)
N1—C4	1.385 (5)	C12—C13	1.343 (6)
N2—C6	1.399 (5)	C17—C18	1.363 (6)
N2—C9	1.347 (6)	C4—C5	1.373 (6)
N3—C11	1.351 (5)	C5—C6	1.370 (6)
N3—C14	1.376 (5)	C9—C10	1.403 (7)
N4—C16	1.391 (5)	C10—C11	1.382 (6)
N4—C19	1.346 (5)	C14—C15	1.375 (6)
C1—C2	1.464 (6)	C15—C16	1.387 (6)
C3—C4	1.440 (6)	C19—C20	1.395 (6)
C6—C7	1.437 (6)	C1—C20	1.381 (6)
C8—C9	1.464 (6)		
N1—Rh—N2	90.5 (1)	N1—C1—C2	109.6 (3)
N1—Rh—N4	89.2 (1)	N1—C4—C3	108.0 (3)
N2—Rh—N3	89.3 (1)	N2—C6—C7	109.0 (4)
N3—Rh—N4	91.0 (1)	N2—C9—C8	112.1 (4)
N1—Rh—N3	178.5 (1)	N3—C11—C12	109.6 (3)
N2—Rh—N4	178.8 (1)	N3—C14—C13	109.2 (3)
N1—Rh—C37	92.5 (2)	N4—C16—C17	109.8 (4)
N2—Rh—C37	90.8 (2)	N4—C19—C18	111.8 (4)
N3—Rh—C37	89.0 (2)	C1—C2—C3	105.9 (4)
N4—Rh—C37	90.4 (2)	C2—C3—C4	108.9 (4)
Rh—N1—C1	126.4 (3)	C6—C7—C8	108.7 (4)
Rh—N1—C4	125.8 (3)	C7—C8—C9	104.2 (4)
Rh—N2—C6	126.1 (3)	C11—C12—C13	106.5 (4)
Rh—N2—C9	127.8 (3)	C12—C13—C14	107.6 (4)
Rh—N3—C11	126.8 (3)	C16—C17—C18	107.5 (4)
Rh—N3—C14	125.9 (3)	C17—C18—C19	105.3 (4)
Rh—N4—C16	126.2 (3)	C2—C1—C20	124.9 (4)
Rh—N4—C19	128.2 (3)	C3—C4—C5	127.1 (4)
C1—N1—C4	107.7 (3)	C5—C6—C7	126.3 (4)
C6—N2—C9	106.1 (3)	C8—C9—C10	123.3 (4)
C11—N3—C14	107.1 (4)	C10—C11—C12	124.8 (4)
C16—N4—C19	105.5 (3)	C13—C14—C15	125.7 (4)
N1—C1—C20	125.6 (4)	C15—C16—C17	125.7 (4)
N1—C4—C5	124.9 (4)	C18—C19—C20	123.6 (4)
N2—C6—C5	124.7 (4)	C4—C5—C6	127.9 (4)
N2—C9—C10	124.6 (4)	C9—C10—C11	125.6 (4)
N3—C11—C10	125.7 (4)	C14—C15—C16	127.4 (4)
N3—C14—C15	125.1 (4)	C19—C20—C1	125.9 (4)
N4—C16—C15	124.4 (4)		
N4—C19—C20	124.6 (4)		

and Table 2 selected bond distances and angles. Fig. 1 shows an *ORTEP* (Johnson, 1976) drawing of the title compound with adopted numbering.

Discussion. A structure (α form) of Rh(oep)(CH₃) has been reported (Takenaka, Syal, Sasada, Omura, Ogoshi & Yoshida, 1976). The present structure (β form) reveals several noticeable differences from the earlier one: (a) the Rh—C distance is significantly shorter [1.970 (4) Å] in the β form than in the α form [2.013 (6) Å], (b) all the ethyl groups except for the disordered one in the β form are oriented toward the methyl group attached to Rh whereas four of the ethyl groups are disordered in the α form, (c) the Rh—Rh distance between the nearest neighbors is 4.67 Å in the β form compared to 7.22 Å in the α form. In this structure the two nearest neighbors, which are related to each other by inversion symmetry, form a 'dimer' where the mean-plane separation is 3.35 Å and the lateral shift of the rings is 3.28 Å (Fig. 2). Strong π - π interaction between the porphyrin rings appears to be responsible for the dimeric structure (Scheidt & Lee, 1987).

Although the average bond parameters of the porphyrin core are close to the typical values of metalloporphyrins (Scheidt, 1978; Hoard, 1975) a careful inspection reveals large variations in bond distances, especially those of Rh—N (2.012–2.043 Å) and N—C_a (1.346–1.399 Å). Two quite distinct sets of N—C_a, C_a—C_b and C_b—C_b bonds are observed: $\langle \text{N—C}_a \rangle_{\text{long}} = 1.388$, $\langle \text{N—C}_a \rangle_{\text{short}} = 1.349$; $\langle \text{C}_a\text{—C}_b \rangle_{\text{long}} = 1.460$, $\langle \text{C}_a\text{—C}_b \rangle_{\text{short}} = 1.438$; $\langle \text{C}_b\text{—C}_b \rangle_{\text{long}} = 1.369$, $\langle \text{C}_b\text{—C}_b \rangle_{\text{short}} = 1.343$ Å (nomenclature from Hoard, 1975). The longer and shorter bonds are arranged in such a way that the porphyrin core has

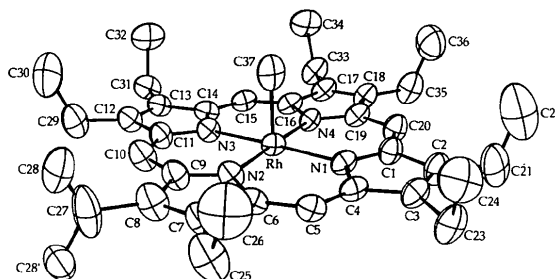


Fig. 1. *ORTEP* (Johnson, 1976) diagram of octaethylporphyrinato(methyl)rhodium(III) (β form) with atom labeling (50% probability thermal ellipsoids). H atoms are omitted for clarity.

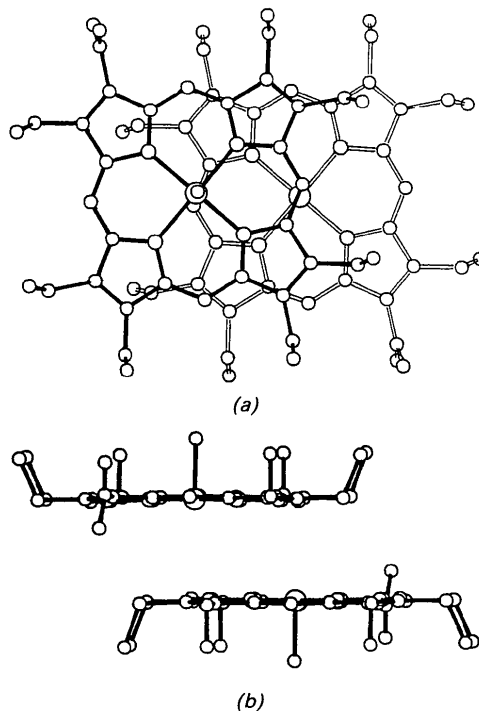


Fig. 2. *PLUTO* (Motherwell & Clegg, 1978) drawings of the two Rh(oep)(CH₃) related by an inversion center showing the overlap of the two cores: (a) top view (the heavy lined core is closer to the viewer), (b) side view.

approximate D_{2h} symmetry. The origin of such a variation in bond distances is not understood. The porphyrin core is essentially planar and the displacement of Rh is only 0.024 Å from the mean four-nitrogen plane toward the methyl group.

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Complexation d'un Agent Trichomonacide (Ténonitrozole) par l'Acétate de Rhodium: Structure Cristalline du Tétrakis(μ -acétato)-bis[5-nitro-2-(2-thénoylamino)-1,3-thiazole]dirhodium(II) Dichlorométhane

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Abstract. $[\text{Rh}(\text{CH}_3\text{CO}_2)_2(\text{C}_8\text{H}_5\text{N}_3\text{O}_3\text{S}_2)]_2 \cdot \text{CH}_2\text{Cl}_2$, $M_r = 1037.5$, monoclinic, $P2_1/n$, $a = 8.074$ (2), $b = 19.088$ (4), $c = 12.007$ (2) Å, $\beta = 95.39$ (2)°, $V = 1842.3$ (1) Å³, $Z = 2$, $D_m = 1.82$ (3), $D_x = 1.86$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $\mu = 1.3$ mm⁻¹, $F(000) = 1032$, $T = 294$ (1) K, $R = 0.028$ for 2323 independent reflections. The unit-cell contains two discrete molecules, which present an inversion centre. In the adduct, the Rh—N bond length of 2.242 (8) Å is slightly shorter than that observed in a complex formed from rhodium acetate and diphenyltriazene. The Rh—Rh distance [2.383 (1) Å] and other parameters for the rhodium acetate cage show no major

deviations from those reported in the complex with diphenyltriazene. In the title complex, the atoms O(27) and S(21) of the thenoyl group are in an *E* conformation relative to the C(22)—C(26) bond, while in the free ligand and its dimethylformamide solvate the corresponding conformation is *Z*.

Introduction. Les carboxylates de rhodium(II) suscitent un intérêt soutenu depuis quelques années, tant pour leurs propriétés catalytiques en synthèse organique, que pour leur action comme agents antitumoraux potentiels, par inhibition de la synthèse de l'ADN (Howard, Kimball & Bear, 1979; Erck,