Synthesis and X-ray Structures of Rhodium Complexes of N^{21}, N^{22}-Bridged Porphyrin

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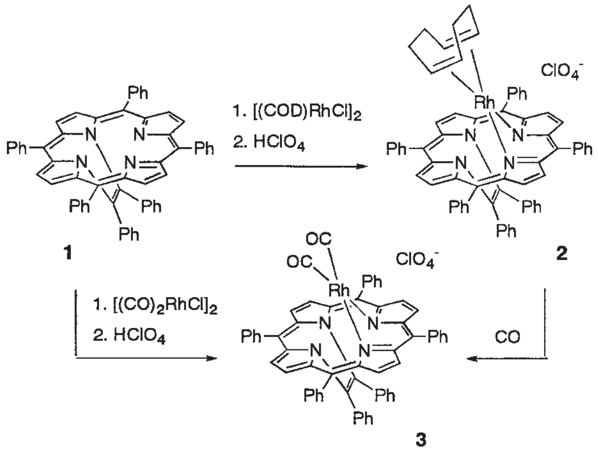
(η^4-1,5-Cyclooctadienyl)rhodium(I) complex with a bidentate N^{21}, N^{22}-bridged porphyrin ligand was prepared. The η^4-1,5-cyclooctadiene ligand was easily replaced by carbon monoxide to give the corresponding (dicarbonyl)rhodium(I) porphyrin. The structures of these two complexes were proven by X-ray crystallography.

In 1973, bidentate coordination mode of porphyrin to rhodium(I) through the monoanionic dipyrrylmethene unit was demonstrated.[1] This sitting-atop type metalloporphyrins where a metal ion is bound over the porphyrin plane have been drawing attention and thus rhodium complexes of porphyrinoids such as corrole, porphyrin, sapphyrins, thiasapphyrin, amethyrin, and related macrocycles have been reported.[1–7] In these complexes a dipyrrylmethene unit and two carbonyl ligands constitute square planar geometry of Rh. Since bis(dicarbonylrhodium)porphyrin is easily converted into a mononuclear rhodium porphyrin with ordinary tetradentate mode of porphyrin,[8b] utility of bidentate mode of porphyrin in organometallic and coordination chemistry has remained unexplored.

It has been shown that single rhodium ion is sitting atop the macrocycle face opposite to the *N*-methyl group in the *N*-methyl corrole.[2] This is because an *N*-alkyl group prevents metal coordination on the same face of the macrocycle plane. However, metallation of *N*-methylporphyrin with $[(CO)_2RhCl]_2$ eventually causes N-to-Rh methyl shift with simultaneous insertion of Rh into the center of porphyrin N_4 core.[8a] We have recently shown that the N^{21}, N^{22}-(etheno) bridge of porphyrin is quite robust and serves for making various organopalladium complexes of a bidentate porphyrin ligand.[9] In this paper is described our effort to extend the scope of coordination chemistry of the N^{21}, N^{22}-(etheno) bridged porphyrin ligand.

The reaction of N^{21}, N^{22}-(1,2-diphenyletheno)tetraphenylporphyrin free base (N^{21}, N^{22}-(PhC = CPh)(TPP)) (**1**) with a slightly excess amount of μ-dichlorobis[(1,5-cyclooctadienyl)-rhodium(I)] ($[(COD)Rh^{I}Cl]_2$) in CH_2Cl_2 at room temperature for 1 h afforded $[N^{21},N^{22}\text{-(PhC = CPh)(TPP)}]Rh^{I}(COD)ClO_4$ (**2**)[10] in 70% yield after shaking the reaction mixture with a 1% $HClO_4$ aqueous solution, chromatographic purification on silica gel, and recrystallization from CH_2Cl_2-diethyl ether. A similar reaction of **1** with $[(CO)_2Rh^{I}Cl]_2$ in benzene gave $[N^{21},N^{22}\text{-(PhC = CPh)-(TPP)}]Rh^{I}(CO)_2ClO_4$ (**3**)[11] in 38% yield. This complex **3** was obtained alternatively in 97% yield by vigorously stirring a CH_2Cl_2 solution of **2** for 30 min under atmospheric pressure of carbon monoxide (Scheme 1). UV-vis spectrum of **2** shows split Soret bands at 424 and 479.5 nm and broad visible bands whereas a sharp Soret band of **3** is seen at 456 nm (see Figure 1). These spectral features reflect different trans effect between COD and CO. The NMR signals of the COD ligand of **2** show up-field shifts owing to the ring current effect of porphyrin. For example, the ^1H chemical shift of the COD olefinic proton at −2.29 ppm is by ca. 6.5 ppm higher than those of the Rh(COD) complexes of diamine ligand.[12–16] The ^{13}C signals of the COD olefinic carbons at 71.1 and 78.1 ppm are well upfield shifted in comparison with those (ca. 80 ppm) of Rh(I)-bound olefin carbons in the literatures,[12–16] whereas the $J_{Rh\text{-}C}$ value (13 Hz) of **2** is typical.[13–16] The $J_{Rh\text{-}C}$ value (69 Hz) of **3** is similar to that reported for the $Rh(CO)_2$ complex of the pyridine containing expanded porphyrin (68 Hz).[6]



Scheme 1.

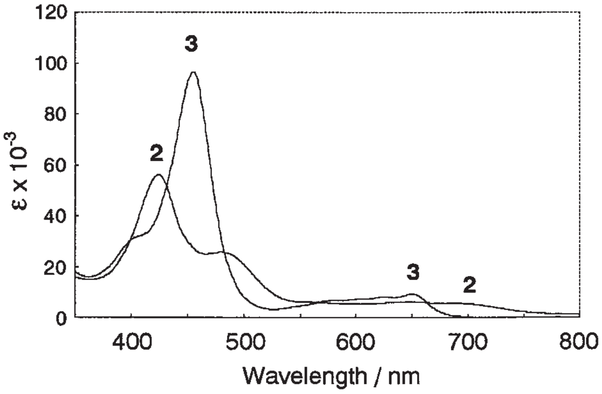


Figure 1. UV-Vis spectra of **2** and **3** in CH_2Cl_2.

The X-ray crystal structures of **2** and **3** clearly show that the Rh(COD) and $Rh(CO)_2$ moieties are on the opposite side to the N^{21}, N^{22}-(PhC = CPh) bridge (see Figure 2 and 3).[17] The N(3)N(4)Rh plane of **3** is canted by 53.5° from the mean porphyrin plane defined by four *meso* carbons, C(5), C(10), C(15), and C(20). This dihedral angle is similar to that (53.4°) observed for (π-allyl)Pd^{II} complex of **1**.[9] This sitting-atop type structure is enabled by the tilting of the ligating pyrrole rings with respect to the mean porphyrin plane. The dihedral angles of the mean pyrrole planes, C(11)C(12)C(13)C(14)N(3) and C(16)C(17)C(18)C(19)N(4), against the mean porphyrin plane are 21.0° and 12.8° for **2** and 18.4° and 15.3° for **3**, respectively.

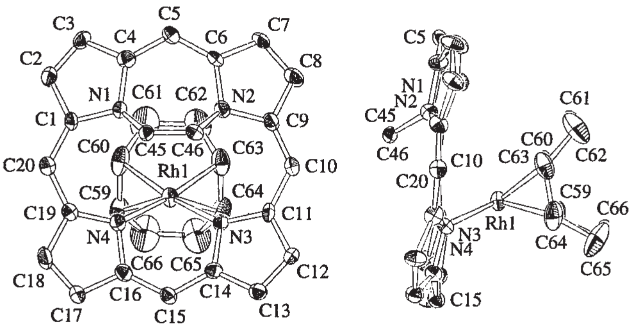


Figure 2. ORTEP drawings of **2** with 30% probability thermal ellipsoids and atom-numbering scheme. Six phenyl groups at C5, C10, C15, C20, C45, and C46, a ClO_4 ion, and a CH_2Cl_2 solvate were omitted for clarity. A side view is shown on the right. Selected distances (Å) and angles (deg): Rh-N3, 2.127(9); Rh-N4, 2.130(8); Rh-C59, 2.14(1); Rh-C60, 2.14(1); Rh-C63, 2.11(1); Rh-C64, 2.11(1); C59-C60, 1.40(2); C60-C61, 1.49(2); C61-C62, 1.45(3); C62-C63, 1.50(2); C63-C64, 1.39(2); C64-C65, 1.52(2); C65-C66, 1.41(3); C59-C66, 1.50(2); N3-Rh-N4, 83.1(3); N3-Rh-C63, 97.5(5); N3-Rh-C64, 89.9(4); N4-Rh-C59, 89.9(4); N4-Rh-C60, 97.3(4); C59-Rh-C64, 82.0(5); C60 Rh-C63, 80.7(5).

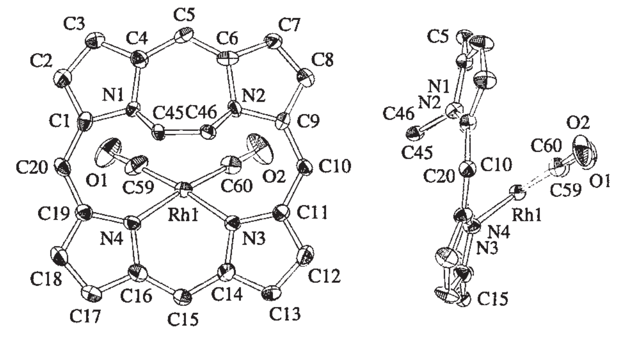


Figure 3. ORTEP drawings of **3** with 30% probability thermal ellipsoids and atom-numbering scheme. Six phenyl groups at C5, C10, C15, C20, C45, and C46, a ClO_4 ion, and a $C_4H_{10}O$ solvate were omitted for clarity. A side view is shown on the right. Selected distances (Å) and angles (deg): Rh-N3, 2.082(9); Rh-N4, 2.092(8); Rh-C59, 1.84(2); Rh-C60, 1.85(1) O1-C59, 1.14(2); O2-C60, 1.13(1); N3-Rh-N4, 83.5(3); N3-Rh-C60, 93.1(5); N4-Rh-C59, 93.0(5); C59-Rh-C60, 90.2(3).

Although the cant of the ligating pyrrole rings is not so different between **2** and **3**, the cant of the N(3)N(4)Rh plane of **2** is by 10.3 ° greater than that of **3**. Furthermore, the midpoints of the C=C bonds of COD do not make a square plane of Rh coordination, as is seen from the dihedral angles of the N(3)N(4)Rh plane against the C(60)C(63)Rh plane (11.5 °) and the C(59)C(64)Rh plane (39.8 °). The shifted coordination of COD to Rh has also been noted in the hydridotris(pyrazolyl)borate complexes but their shifts of COD are less than that in the present case.[14,15] These structural features of **2** should be explained in terms of steric repulsion between COD and porphyrin.

The complex **2** is the first example of Rh-olefin complex of porphyrinoid, while $(CO)_2Rh$ porphyrinoids have been well known.[1–7] The N^{21},N^{22}-(etheno) bridge maintains bidentate mode of porphyrin for Rh coordination and steric repulsion between the COD ligand and the porphyrin ligand can be relieved by changing deviation of the Rh atom from the porphyrin ligand.

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10 **2**: Yield 70%; ^{1}H NMR (δ, $CDCl_3$): 9.17, 8.86, 8.71, 8.15 ($d \times 4$, 2H × 4, pyrrole-β-H); 8.5–7.0 (m, 20H, *meso*-phenyl-H); 6.19 (t, 2H, bridge phenyl-*p*-H); 5.80 (very broad, 4H, bridge phenyl-*m*-H); 0.58, −0.06, −0.70, −1.71 (m × 4, 2H × 4, CH_2); 0.10, −2.29 (m × 2, 2H × 2, -CH =); ^{13}C NMR (δ, $CDCl_3$): 71.7, 78.1 (-CH =, $J_{Rh\text{-}C} = 13$ Hz); 26.9, 28.5 (CH_2). UV/Vis (CH_2Cl_2): $\lambda_{max}(\log \varepsilon)$ 339.5 (4.16), 424 (4.75), 479.5 (4.41), 562 (3.71), 645 (3.74), 695 (3.67) nm. MS (ESI in MeOH): *m*/*z* 1001.381 (calcd for $C_{66}H_{50}N_4Rh$ (M-ClO_4): 1001.309).

11 **3**: Yield 97%; ^{1}H NMR (δ, $CDCl_3$): 9.33, 8.93, 8.82, 8.27 (d × 4, 2H × 4, pyrrole-β-H); 8.4 ~ 7.4 (m, 20H, *meso*-phenyl-H); 6.25 (t, 2H, bridge phenyl-*p*-H); 5.84 (broad, 4H, bridge phenyl-*m*-H); 2.0 (broad, 4H, bridge phenyl-*o*-H); ^{13}C NMR (δ, $CDCl_3$): 177.2 (Rh-CO, $J_{Rh\text{-}C} = 69$ Hz). IR (KBr) 2076, 2004 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max}(\log \varepsilon)$ 339 (4.33), 456 (4.98), 604.5 (3.91), 626 (3.95), 650.5 (4.01) nm. MS (ESI in MeOH): m/z 949.236 (calcd for $C_{60}H_{38}N_4O_2Rh$ (M-ClO_4): 949.204).

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17 Crystal data. **2**: $C_{66}H_{50}ClN_4O_4Rh\cdot(1/2)CH_2Cl_2$, $M = 1143.97$, triclinic, space group $P-1$ (#2), $a = 12.699(3)$, $b = 17.997(5)$, $c = 12.336(2)$ Å, $\alpha = 97.31(2)$, $\beta = 90.27(2)$, $\gamma = 79.33(2)°$, $V = 2747.4(12)$ Å^3, $Z = 2$, $D_{calc} = 1.38$ g/cm^3, μ(Mo-Kα) = 4.61 cm^{-1}, $T = 294$ K, crystal size 0.1 × 0.2 × 0.03 mm. A total of 4370 with $I > 3.00\sigma(I)$ out of 7517 unique reflections ($4 < 2\theta < 50°$) were collected. The refinement of 671 parameters on F_o converged at $R = 0.069$, $R_w = 0.069$, and GOF = 1.72. **3**: $C_{60}H_{38}ClN_4O_6Rh\cdot(C_4H_{10}O)$, $M = 1123.46$, triclinic, space group $P-1$ (#2), $a = 14.053(3)$, $b = 16.848(5)$, $c = 12.238(3)$ Å, $\alpha = 98.49(2)$, $\beta = 90.65(2)$, $\gamma = 108.41(2)°$, $V = 2713.9(12)$ Å^3, $Z = 2$, $D_{calc} = 1.37$ g/cm^3, μ(Mo-Kα) = 4.22 cm^{-1}, $T = 290$ K, crystal size 0.6 × 0.2 × 0.03 mm. A total of 4252 with $I > 3.00\sigma(I)$ out of 12164 unique reflections ($4 < 2\theta < 55°$) were collected. The refinement of 646 parameters on F_o converged at $R = 0.075$, $R_w = 0.076$, and GOF = 1.58.