

## Syntheses and Reactions of Hydridorhodium(III) Octaethylporphyrin and Rhodium(II) Octaethylporphyrin Dimer †

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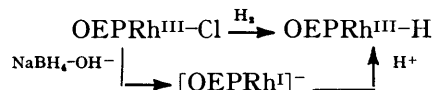
Hydridorhodium(III) octaethylporphyrin, (OEP)Rh<sup>III</sup>-H (1), was formed by the introduction of hydrogen gas into a methanol solution of (OEP)Rh<sup>III</sup>-Cl or by the acidification of the (OEP)Rh<sup>I</sup> anion in alcoholic solution. Complex (1) when degassed to liberate hydrogen or aerially oxidized in benzene gave a dimeric complex with Rh-Rh bonding which was formulated as [(OEP)Rh<sup>II</sup>]<sub>2</sub> (2). The reaction of (2) with alkyl halides, unactivated olefins, and acetylenes occurred smoothly to afford organorhodium(III)-OEP complexes (3)-(11).

As part of our studies on metalloporphyrins we have already elucidated the reaction behaviour of rhodium-(I) and -(III) complexes of octaethylporphyrin.<sup>1-4</sup> Low-valent rhodium complexes of  $\alpha\beta\gamma\delta$ -tetraphenylmesoporphine, (TPP)H<sub>2</sub>, have been reported by James and Stynes, who characterized a rhodium(II) complex as a monomeric compound on the basis of the magnetic moment and the e.s.r. signals; this, in spite of the tendency of rhodium(II) complexes to form a metal-metal bond.<sup>5-7</sup> They also formulated a rhodium(I) complex which was obtained by reduction of (TPP)Rh<sup>II</sup> with hydrogen as H<sup>+</sup>[(TPP)Rh<sup>I</sup>]<sup>-</sup>·2H<sub>2</sub>O.<sup>8</sup> It is well known that the redox potentials of the central metal, and also of the porphyrin ring, in metalloporphyrins vary with the nature of substituent groups at the periphery of the porphyrin ring.<sup>9</sup> This means that the chemical behaviour and spectral properties of metalloporphyrins differ according to the structure of porphyrin. The difference in electronic and steric effect between TPP and OEP is especially remarkable, as illustrated by the fact that the e.s.r. and optical spectra of  $\pi$ -cation radicals of Mg<sup>II</sup> complexes of TPP and OEP are different from each other because the energy levels of the two HOMOs (*a<sub>1u</sub>* and *a<sub>2u</sub>*) in the porphyrin  $\pi$ -system are reversed between TPP and OEP.<sup>10</sup> In this work, the chemical properties of the rhodium complex of an ET10-type porphyrin such as octaethylporphyrin have been found to be notably different from those of the rhodium complex of tetraphenylmesoporphine. The first synthesis of the hydridometalloporphyrin, (OEP)Rh<sup>III</sup>-H (1), and the dimeric complex [(OEP)Rh<sup>II</sup>]<sub>2</sub> (2), is described below together with novel reactions of the latter.

### RESULTS AND DISCUSSION

Introduction of hydrogen into a methanol solution of (OEP)Rh<sup>III</sup>-Cl resulted in the formation of a deep orange precipitate of (OEP)Rh<sup>III</sup>-H (1), which showed an intense, sharp absorption at 2 220 cm<sup>-1</sup> in the i.r.-region assignable to the Rh-H stretching vibration. When an alkaline alcoholic solution of the anionic complex,<sup>1</sup> [(OEP)Rh<sup>I</sup>]<sup>-</sup>, generated by the reduction of

(OEP)Rh<sup>III</sup>-Cl with NaBH<sub>4</sub> under basic conditions was acidified with acetic acid, the same complex was obtained in 80% yield. Upon acidification by using CH<sub>3</sub>-CO<sub>2</sub>D in the latter procedure, a new band due to the Rh-D stretching vibration appears at 1 595 cm<sup>-1</sup>. A benzene solution of (1) under strictly degassed conditions shows a visible spectrum which is identical with those of alkylrhodium(III)-OEP complexes,<sup>1</sup> indicating that the rhodium in complex (1) exists as Rh<sup>III</sup>. The <sup>1</sup>H n.m.r. spectrum of (1) in degassed [<sup>2</sup>H<sub>5</sub>]pyridine shows a signal due to the metal-bound proton at  $\delta$  -32.99 split by <sup>103</sup>Rh (*I* = 1/2), with a coupling constant of 22.5 Hz. Protons bonded to Rh<sup>III</sup> in the cationic complex [Rh<sup>III</sup>-H<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(MeCN)<sub>2</sub>]<sup>+</sup> were reported to resonate at  $\delta$  -17.4 with *J*<sub>Rh-H</sub> 17.0 Hz.<sup>11</sup> The additional upfield



shift in the case of complex (1) in comparison with this cationic complex is ascribable to the diamagnetic ring current effect and the electron-donating effect of the porphyrin ligand. The upfield shift due to the ring current can be reasonably evaluated to be *ca.* 10 p.p.m. if the Rh-H bond length is assumed to be *ca.* 2 Å.<sup>1</sup> Eight ethyl groups at the periphery of the porphyrin ring stabilizes the higher oxidation state of the central metal. Therefore, the Rh-H bond of (1) seems to be more covalent than that of the corresponding tetraphenylporphine complex, H<sup>+</sup>[(TPP)Rh<sup>I</sup>]<sup>-</sup> characterized by James and Stynes.<sup>8</sup>

When complex (1) was dissolved in non-degassed benzene, the colour of the solution changed from orange to brown, indicating the formation of [(OEP)Rh<sup>II</sup>]<sub>2</sub> (2). Figure 1 shows the change in the visible spectrum of a 1.16 mM benzene solution of (1) during 2 h after dissolution. The intensities of the Soret band at 397 nm and the visible bands at 512 and 543 nm simultaneously decrease, and the Soret band splits into two bands at 352 and 388 nm with four isosbestic points at 368, 425, 497, and 553 nm. When a saturated hot toluene solution of (1) was left in contact with air, reaction occurred rapidly and dark violet crystals of (2) were obtained on cooling.

† Preliminary communication; J. Setsune, Z. Yoshida, and H. Ogoshi, *J. Am. Chem. Soc.*, 1977, **99**, 3869.

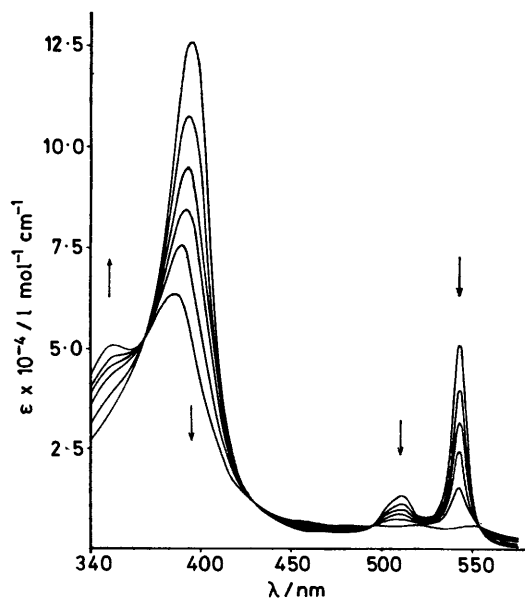
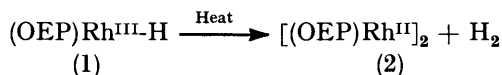
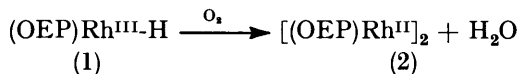


FIGURE 1 Visible spectrum change:  $(\text{OEP})\text{Rh}^{\text{III}}\text{-H} \rightarrow [(\text{OEP})\text{Rh}^{\text{II}}]_2$

While oxidative cleavage of the Rh-H bond was found to be an effective reaction pathway to give (2), we have also confirmed that homolytic cleavage of the Rh-H bond takes place in a kinetically slower process to afford (2) with concomitant liberation of hydrogen gas (detected by g.l.c. analysis of the gas from the reaction vessel) when complex (1) was heated at 70 °C in degassed toluene for one week.



The  $^1\text{H}$  n.m.r. spectrum of (2) shows four equivalent meso-protons at  $\delta$  9.26, peripheral methylene protons at

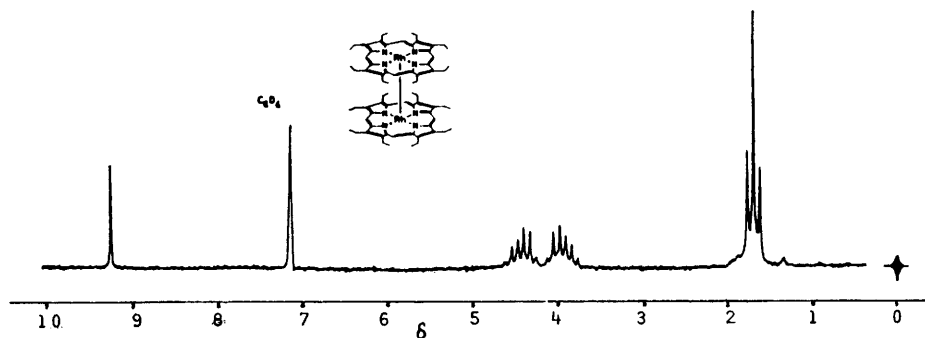


FIGURE 2  $^1\text{H}$  N.m.r. spectrum of  $[(\text{OEP})\text{Rh}^{\text{II}}]_2$  (2)

$\delta$  4.45 and 3.95 in an  $\text{ABX}_3$  pattern, and peripheral methyl protons at  $\delta$  1.71 as shown in Figure 2. This spectrum is quite similar to that of the metal-metal bonded dimeric ruthenium complex,  $[(\text{OEP})\text{Ru}^{\text{II}}]_2$ , reported by Whitten.<sup>13</sup> It should be noted that the diastereotopic

nature of the peripheral methylene protons is clearly illustrated in the spectra of both (2) and  $[(\text{OEP})\text{Rh}^{\text{II}}]_2$ , which provides the best evidence in support of the dimeric structure of (2). This formulation also explains the sharp signals in the spectrum of (2), in terms of the spin pairing of odd  $d$ -electrons from two  $d^7$  rhodium(II) ions *via* metal-metal bonding. The formulation of (2) as a dimer was further supported by the magnetic susceptibility ( $\chi = -0.65 \times 10^{-6}$  at 25 °C) indicating its diamagnetic character, and by the absence of Rh-H absorption in the i.r. spectrum measured in benzene solution. In the case of rhodium(II) porphyrins, the effect of substituents at the periphery of the porphyrin ring is noteworthy. The preference for a monomeric structure in  $(\text{TPP})\text{Rh}^{\text{II}}$  seems to result from steric constraints of the meso-phenyl groups, which would be very crowded in the dimer.

Many complexes containing metal-metal bonds are known, with various bond lengths according to the bond order. Single-crystal  $X$ -ray studies of some dinuclear  $\text{Rh}^{\text{II}}$  compounds have revealed that  $[\text{Rh}^{\text{II}}(\text{DMG})_2\text{PPh}_3]_2$  has a single Rh-Rh bond with a length of 2.934 Å,<sup>5</sup> and the Rh-Rh bond distance in  $\text{Rh}^{\text{II}}_2(\text{OCOME})_4(\text{H}_2\text{O})_2$  is 2.45 Å, implying multiple bonding.<sup>14</sup> If we assume  $D_{4h}$  molecular symmetry for complex (2), two porphyrin ligands are eclipsed and a triple bond is expected, while only a single bond is possible for the staggered conformation ( $D_{4d}$  symmetry). In any case the distance between the two porphyrin planes is considered to be *ca.* 3 Å to permit  $\pi$ - $\pi$  interaction of the two porphyrin ligands. The fact that the electronic spectrum of the dimer (2) is notably different from those of normal metalloporphyrins ‡ is explained in terms of the change in energy of the  $\pi \rightarrow \pi^*$  transition, together with the  $\pi \rightarrow d$  and  $d \rightarrow \pi^*$  transitions, which are considered to have a significant intensity in association with the  $\pi \rightarrow \pi^*$  transition.<sup>15</sup>

Hydridocobal(III)oxime and hydridorhod(III)oxime are hydridometal complexes with a macrocyclic square-planar ligand system.<sup>16,17</sup> Schrauzer reported that these

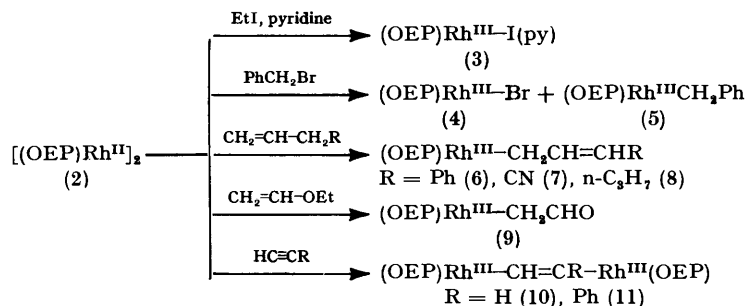
hydrido-complexes afforded organo-cobal(III) and -rhodium(III) complexes on treatment with alkyl halides

‡ The rhodium(II) metalloporphyrins generally show a strong absorption at *ca.* 400 nm ( $\epsilon$  2–5  $\times 10^5$ ) and two visible bands at *ca.* 550 nm ( $\epsilon$  1–5  $\times 10^4$ ).

and electron-deficient olefins. However, formation of metal(II) complexes from these hydrido-compounds has not been found. In contrast to the reaction behaviour of hydridorhodium(III) octaethylporphyrin (1) failed to give organorhodium(III)-OEP which, on the other hand, was effectively prepared from the Rh<sup>II</sup> complex (2). Some cobalt(II) complexes including cobal(II)oxime have been known to react with alkyl halides and acetylenes to give organocobalt complexes,<sup>18-22</sup> while the reaction with olefins gives ambiguous

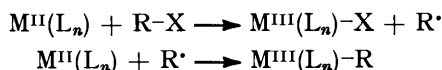
(2) and ethyl vinyl ether. Treatment of complex (2) with acetylene and phenylacetylene afforded the bridged complexes (10) and (11), respectively, in *ca.* 70% yield. Absorptions due to the vinyl or phenyl protons in their <sup>1</sup>H n.m.r. spectra appear at much higher field than those of β-*cis*-styrylrhodium(III)-OEP<sup>1</sup> because of the enhanced ring-current effect from two porphyrin rings.

When complex (2) was allowed to react with olefins substituted with electron-withdrawing groups, the oxidation state of rhodium changed from II to III without the



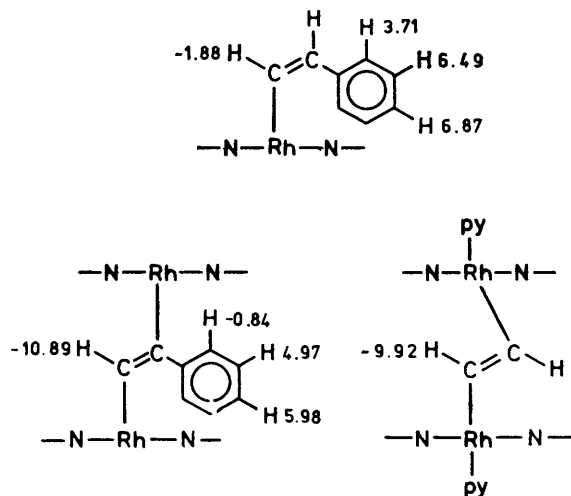
SCHEME 1 Reactions of  $[(\text{OEP})\text{Rh}^{\text{II}}]_2$  (2)

results.<sup>23</sup> The Rh-C bond was generated easily when a benzene solution of complex (2) was treated with various organic substrates under argon (Scheme 1). Although (OEP)Rh<sup>III</sup>-I(py) (3) and only a trace amount of alkylrhodium(III)-OEP were isolated in the reaction of (2) with ethyl iodide, (OEP)Rh<sup>III</sup>-Br (4) and (OEP)Rh<sup>III</sup>-CH<sub>2</sub>Ph (5) were formed in 39 and 26% yield, respectively, when an excess of benzyl bromide was used. The abstraction of a bromine radical from benzyl bromide and the capture of a benzyl radical resulted in the formation of (4) and (5) *via* the same mechanism established for Co<sup>II</sup> complexes.<sup>18,19</sup> Complex (2) reacted rapidly with



allylic compounds such as allylbenzene, allyl cyanide, and hex-1-ene to give (3-substituted-prop-2-enyl)rhodium(III)-OEP complexes, (6), (7), and (8), in moderate yields. The vicinal coupling constant of olefinic protons (16 Hz) indicates a *trans*-olefin configuration for the cinnamyl complex (6). On the other hand, the <sup>1</sup>H n.m.r. spectrum of the cyano-derivative (7) showed that it consisted of a *cis* and *trans* mixture (*cis:trans* ratio 1:2), which has not yet been separated by chromatography. The <sup>1</sup>H n.m.r. spectrum did not give clear evidence as to the structure of the olefin moiety of the hexenyl complex (8). Methylene protons bonded directly to Rh in the complexes (6), (7), and (8) resonate at  $\delta$  *ca.* -5 coupled with both <sup>103</sup>Rh and vicinal vinylic proton, which supports an S<sub>H2</sub> reaction mechanism, *i.e.* the addition of Rh<sup>II</sup> to the terminal carbon of the olefin, followed by elimination of a hydrogen radical from the allylic position with simultaneous migration of the double bond. A similar reaction mode can rationalize the formation of (formylmethyl)rhodium(III)-OEP (9) from

formation of a Rh<sup>III</sup>-C bond, suggesting rapid electron transfer from metal to olefin. Rhodium-porphyrin complexes have also not been generated by treatment with dimethyl acetylenedicarboxylate. These observations indicate that organorhodium complexes are not



#### Chemical shifts ( $\delta$ ) of the axial organic groups

formed *via* an electron-transfer process but, rather, *via* the intermediate formation of an olefin  $\pi$ -complex of Rh<sup>II</sup>(OEP) where electron-donation from the olefin to rhodium(II) plays an important role.

#### EXPERIMENTAL

I.r. spectra were recorded using KBr disks on a Hitachi EPI-G31 grating spectrophotometer; <sup>1</sup>H n.m.r. spectra were recorded on a Varian HA-100 spectrometer using

tetramethylsilane as internal reference; visible spectra were recorded on a Hitachi EPS-3T recording spectrophotometer. Magnetic susceptibilities were measured by a modified Gouy method at 25 °C. A Shimadzu gas chromatograph GC-4B system was used for gas analysis. Chloro-octaethylporphyrinorhodium(III) was prepared according to the published method.<sup>1</sup> Kieselgel 60 F<sub>254</sub> (Merck) was used for thin layer chromatography. Wakogel C-200 (Wako Junyaku) was used for column chromatography.

(OEP)Rh<sup>III</sup>-H (1).—(A) (OEP)Rh<sup>III</sup>-Cl (100 mg) was dissolved in ethanol (30 ml) at 50 °C, NaBH<sub>4</sub> (20 mg) in aqueous 1M-NaOH solution (2 ml) was added and the mixture was stirred for 2 h under argon at 50 °C. After the solution had cooled to room temperature, acetic acid (5 ml) was added, resulting in the immediate formation of a deep orange precipitate. Water (20 ml) was added to the mixture and the precipitate was filtered off and dried over P<sub>2</sub>O<sub>5</sub> *in vacuo* at 80 °C to give (OEP)Rh<sup>III</sup>-H (1) in 80% yield;  $\nu_{\max}$ . 2 220 cm<sup>-1</sup> (Rh-H);  $\delta$ (C<sub>5</sub>D<sub>5</sub>N) -32.99 (d, Rh-H,  $J_{\text{Rh-H}}$  22.5 Hz) (Found: C, 67.95; H, 7.25; N, 8.75. Calc. for C<sub>36</sub>H<sub>45</sub>N<sub>4</sub>Rh: C, 67.91; H, 7.12; N, 8.80%).

(B) When hydrogen was introduced into a methanol solution of (OEP)Rh<sup>III</sup>-Cl, a deep orange precipitate was formed in 10 min. This was filtered off and dried to give (OEP)Rh<sup>III</sup>-H (1) in 19% yield.

Complex [(OEP)Rh<sup>III</sup>]<sub>2</sub> (2).—(OEP)Rh<sup>III</sup>-H (1) (334 mg) was suspended in toluene (20 ml) under argon. When the mixture was heated to 90 °C, complex (1) dissolved; the stopcock was then opened and the solution allowed into contact with air for 1 min. The colour of the solution turned rapidly from orange to brown. The hot solution was cooled and allowed to stand overnight in a refrigerator to give 285 mg of dark violet crystals, which were filtered off and washed with light petroleum in a stream of argon to afford [(OEP)Rh<sup>III</sup>]<sub>2</sub>·C<sub>7</sub>H<sub>8</sub> (2) in 79% yield:  $\delta$ (C<sub>6</sub>D<sub>6</sub>) 9.26 (s, 8 H, 8% =CH-), 7.03 (m, 5 H, *PhMe*), 4.45 and 3.95 (both dq, 32 H, 16 × CH<sub>2</sub>Me), 2.10 (s, 3 H, *PhMe*), and 1.71 (16 × CH<sub>2</sub>Me);  $\lambda_{\max}$ . (benzene) 352 (log  $\epsilon$  5.01), 388 (5.09), 521 (3.77), and 550 nm (3.76); magnetic susceptibility -0.65 × 10<sup>-6</sup> at 25 °C (Found: C, 69.9; H, 7.2; N, 8.25. Calc. for C<sub>72</sub>H<sub>88</sub>N<sub>8</sub>Rh<sub>2</sub>·C<sub>7</sub>H<sub>8</sub>: C, 69.59; H, 7.09; N, 8.22%).

Detection of H<sub>2</sub> Gas.—(OEP)Rh<sup>III</sup>-H (1) (150 mg) and benzene (1 ml) were deaerated in a glass tube by a repeated freeze-thaw process. The tube was then sealed *in vacuo* and the mixture heated at 70 °C for a week. A sample of the gas in the glass tube was drawn into a syringe and injected into a column of molecular sieve (5A) at 50 °C. Nitrogen gas was used as carrier gas with a pressure of 1.0 kg cm<sup>-2</sup>. The existence of H<sub>2</sub> gas in the sample was confirmed by the retention time, which was identical with that of an authentic sample.

Complex (OEP)Rh<sup>III</sup>-I(py) (3).—To complex (2) (55 mg) dissolved in benzene (15 ml) under argon was added ethyl iodide (0.2 ml). The colour of the solution turned instantly from brown to dark red. The solvent was removed under reduced pressure and the resulting residue was chromatographed on a preparative t.l.c. plate with CHCl<sub>3</sub>. The chloroform solution was evaporated and crystallization of the residue from n-hexane-pyridine gave red crystals of (OEP)Rh<sup>III</sup>-I(py) (3) (27 mg, 37%);  $\delta$ (CDCl<sub>3</sub>) 10.14 (s, 4 H, 4 × =CH-), 5.70 (t, 1 H, pyridine  $\gamma$ -H), 4.78 (t, 2 H, 2 × pyridine  $\beta$ -H), 4.09 (q, 16 H, 8 × CH<sub>2</sub>Me), 1.92 (t, 24 H, 8 × CH<sub>2</sub>Me), and 0.50 (d, 2 H, 2 × pyridine  $\alpha$ -H);  $\lambda_{\max}$ . (CHCl<sub>3</sub>) 353 (log  $\epsilon$  4.43), 414 (5.03), 525 (4.21), and 556 nm (4.38) (Found: C, 58.7; H, 5.95; N, 8.35; I, 15.6.

Calc. for C<sub>41</sub>H<sub>49</sub>IN<sub>5</sub>Rh: C, 58.50; H, 5.87; N, 8.32; I, 15.08%).

Complexes (OEP)Rh<sup>III</sup>-Br (4) and (OEP)Rh<sup>III</sup>-CH<sub>2</sub> (5).—Benzyl bromide (45 mg) was added to a benzene solution of complex (2) (84 mg) under argon and the mixture was stirred for 1 h at room temperature. Solvent was then removed and the residue was chromatographed on silica gel. The first orange band eluted with benzene afforded (OEP)-Rh<sup>III</sup>-CH<sub>2</sub>Ph (5) (26 mg, 26%);  $\delta$ (CDCl<sub>3</sub>) 9.64 (s, 4 H, 4 × =CH-), 6.06 (t, 1 H, *Ph para*-H), 5.45 (t, 2 H, 2 × *Ph meta*-H), 3.85 (q, 16 H, 8 × CH<sub>2</sub>Me), 2.32 (d, 2 H, 2 × *Ph ortho*-H), 1.82 (t, 24 H, 8 × CH<sub>2</sub>Me), and -4.64 (d, 2 H, Rh-CH<sub>2</sub>,  $J_{\text{Rh-H}}$  4 Hz);  $\lambda_{\max}$ . (benzene) 390 (log  $\epsilon$  5.06), 513 (4.07), and 544 nm (4.56) (Found: C, 70.95; H, 7.05; N, 7.75. Calc. for C<sub>48</sub>H<sub>51</sub>N<sub>4</sub>Rh: C, 71.06; H, 7.07; N, 7.71%). The second red band eluted with chloroform gave (OEP)Rh<sup>III</sup>-Br (4) in 39% yield;  $\lambda_{\max}$ . (CHCl<sub>3</sub>) 403 (log  $\epsilon$  5.08), 520 (4.14), and 552 nm (4.43) (Found: C, 58.75; H, 6.25; N, 7.45; Br, 11.65. Calc. for C<sub>36</sub>H<sub>44</sub>BrN<sub>4</sub>Rh·H<sub>2</sub>O: C, 58.94; H, 6.32; N, 7.64; Br, 10.89%).

Complex (OEP)Rh<sup>III</sup>-CH<sub>2</sub>CH=CHR [R = Ph (6), CN (7), n-C<sub>3</sub>H<sub>7</sub> (8)].—Complex (2) in benzene was treated with a 3-substituted propene under argon. The products were purified by column chromatography on silica gel using benzene as eluant. (OEP)Rh<sup>III</sup>-CH<sub>2</sub>CH=CHPh (6) was obtained in 57% yield from the reaction with allylbenzene:  $\delta$ (CDCl<sub>3</sub>) 9.95 (s, 4 H, 4 × =CH-), 6.87 (m, 3 H, *Ph*, 2 × *meta*-H + *para*-H), 5.91 (m, 2 H, 2 × *Ph ortho*-H), 3.90 (q, 16 H, 8 × CH<sub>2</sub>Me), 2.41 (d, 1 H, =CHPh), 1.81 (t, 24 H, 8 × CH<sub>2</sub>Me), 0.28 (dt, 1 H, -CH<sub>2</sub>CH=,  $J_{\text{trans}}$  16 Hz), and -4.81 (dd, 2 H, Rh-CH<sub>2</sub>,  $J_{\text{Rh-H}}$  4 Hz);  $\lambda_{\max}$ . (CHCl<sub>3</sub>) 389 (log  $\epsilon$  5.17), 513 (4.08), and 545 nm (4.47) (Found: C, 71.55; H, 7.0; N, 7.55. Calc. for C<sub>45</sub>H<sub>53</sub>N<sub>4</sub>Rh: C, 71.79; H, 7.10; N, 7.44%).

Complex (OEP)Rh<sup>III</sup>-CH<sub>2</sub>CH=CHCN (7) was obtained from the reaction with allyl cyanide (57%). Although t.l.c. showed only one component, the n.m.r. spectrum shows it to be a mixture of *cis*- and *trans*-isomers. The signals due to the *cis*-form appear at  $\delta$  9.73 (s, 4 H, 4 × =CH-), 3.86 (q, 16 H, 8 × CH<sub>2</sub>Me), 2.26 (d, 1 H, =CHCN,  $J_{\text{cis}}$  10 Hz), 1.82 (t, 24 H, 8 × CH<sub>2</sub>Me), -0.35 (dt, 1 H, CH<sub>2</sub>CH=), and -5.17 (dd, 2 H, Rh-CH<sub>2</sub>,  $J_{\text{Rh-H}}$  4 Hz). The signals due to the *trans*-form appear at  $\delta$  9.71 (s, 4 H, 4 × =CH-), 3.86 (q, 16 H, 8 × CH<sub>2</sub>Me), 1.82 (t, 24 H, 8 × CH<sub>2</sub>Me), 0.88 (d, 1 H, =CHCN,  $J_{\text{trans}}$  16 Hz), 0.14 (dt, 1 H, -CH<sub>2</sub>CH=), and -5.46 (dd, 2 H, Rh-CH<sub>2</sub>,  $J_{\text{Rh-H}}$  4 Hz). The C≡N stretching vibration appear at 2 210 cm<sup>-1</sup> in the i.r. spectrum of (7);  $\lambda_{\max}$ . (CHCl<sub>3</sub>) 387 (log  $\epsilon$  5.23), 512 (4.14), and 545 nm (4.61) (Found: C, 68.2; H, 6.9; N, 9.94. Calc. for C<sub>40</sub>H<sub>48</sub>N<sub>5</sub>Rh: C, 68.46; H, 6.89; N, 9.98%). The reaction with hex-1-ene afforded (OEP)Rh<sup>III</sup>-CH<sub>2</sub>CH=CH-C<sub>3</sub>H<sub>7</sub>-n (8) in 38% yield;  $\delta$ (CDCl<sub>3</sub>) 9.91 (s, 4 H, 4 × =CH-), 4.08 (q, 16 H, 8 × CH<sub>2</sub>Me), 1.99 (t, 24 H, 8 × CH<sub>2</sub>Me), 1.67 (m, 1 H, =CHC<sub>3</sub>H<sub>7</sub>), 0.31 (m, 3 H, CH<sub>2</sub>CH<sub>2</sub>Me), 0.20 (m, 1 H, Rh-CH<sub>2</sub>CH=), 0.08 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>Me), -0.37 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>Me), and -5.00 (dd, 2 H, Rh-CH<sub>2</sub>,  $J_{\text{Rh-H}}$  3.5 Hz);  $\lambda_{\max}$ . (CHCl<sub>3</sub>) 390 (log  $\epsilon$  5.12), 514 (4.05), and 545 nm (4.44) (Found: C, 70.15; H, 7.8; N, 7.55. Calc. for C<sub>42</sub>H<sub>55</sub>N<sub>4</sub>Rh: C, 70.18; H, 7.71; N, 7.79%).

Complex (OEP)Rh<sup>III</sup>-CH<sub>2</sub>CHO (9).—When complex (2) was treated with ethyl vinyl ether in benzene under argon, (formylmethyl)rhodium(III)-OEP was obtained in 54% yield by a similar procedure to that described above:  $\nu_{\max}$ . 2 710 and 1 680 cm<sup>-1</sup> (CHO);  $\delta$ (CDCl<sub>3</sub>) 9.97 (s, 4 H, 4 × =CH-), 3.99 (q, 16 H, 8 × CH<sub>2</sub>Me), 2.90 (t, 1 H, CHO,  $J_{\text{vic}}$

5 Hz), 1.86 (t, 24 H,  $8 \times \text{CH}_2\text{Me}$ ), and  $-5.55$  (dd, 2 H,  $\text{Rh}-\text{CH}_2$ ,  $J_{\text{Rh}-\text{H}}$  4 Hz);  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ) 386 (log  $\epsilon$  5.29), 512 (4.25), and 544 nm (4.65) (Found: C, 66.95; H, 6.85; N, 8.3. Calc. for  $\text{C}_{38}\text{H}_{47}\text{N}_4\text{ORh}$ : C, 67.24; H, 6.98; N, 8.26%).

**Complex** (OEP)Rh<sup>III</sup>-CH=CR-Rh<sup>III</sup>(OEP) [R = H (10) and Ph (11)].—An excess of acetylene gas was introduced into a benzene solution of complex (2). The solution was stirred for one day at room temperature to give a red precipitate. This was collected and recrystallized from chloroform containing 5% pyridine to give purple crystals. These when washed with pyridine and dried *in vacuo* afforded the bis-pyridine adduct of (OEP)Rh<sup>III</sup>-CH=CH-Rh<sup>III</sup>(OEP) (10) in 69% yield:  $\delta(\text{CDCl}_3-5\%$  pyridine) 8.95 (s, 8 H,  $8 \times =\text{CH}-$ ), 3.72 (q, 32 H,  $16 \times \text{CH}_2\text{Me}$ ), 1.80 (t, 48 H,  $16 \times \text{CH}_2\text{Me}$ ), and  $-9.92$  (d, 2 H,  $2 \times \text{Rh}-\text{CH}=\text{}$ ,  $J_{\text{Ph}-\text{H}}$  2 Hz);  $\lambda_{\text{max}}$  ( $\text{CHCl}_3-5\%$  pyridine) 402 (log  $\epsilon$  5.43), 520 (4.49), and 552 nm (4.73) (Found: C, 69.1; H, 7.1; N, 9.5. Calc. for  $\text{C}_{84}\text{H}_{100}\text{N}_{10}\text{Rh}_2$ : C, 69.31; H, 6.93; N, 9.62%).

When phenylacetylene was allowed to react with complex (2) in benzene under argon, (OEP)Rh<sup>III</sup>-CH=CC<sub>6</sub>H<sub>5</sub>-Rh<sup>III</sup>(OEP) (11) was generated in 70% yield:  $\delta(\text{CDCl}_3)$  9.05 and 8.92 (both s, 8 H,  $8 \times =\text{CH}$ ), 5.98 (t, 1 H, phenyl *para*-H), 4.96 (t, 2 H, s  $\times$  phenyl *meta*-H), 3.79 (q, 32 H,  $16 \times \text{CH}_2\text{Me}$ ), 1.67 (t, 48 H,  $16 \times \text{CH}_2\text{Me}$ ),  $-0.87$  (d, 2 H,  $2 \times$  phenyl *ortho*-H), and  $-10.97$  (d, 1 H,  $\text{Rh}-\text{CH}=\text{}$ ,  $J_{\text{Rh}-\text{H}}$  2.5 Hz);  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ) 388 (log  $\epsilon$  5.37), 398 (5.45), 518 (4.45), and 550 nm (4.82) (Found: C, 69.65; H, 6.9; N, 7.95. Calc. for  $\text{C}_{80}\text{H}_{94}\text{N}_8\text{Rh}_2$ : C, 69.96; H, 6.90; N, 8.15%).

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