

Meso-Substitution Reactions of Rhodium(III)-Octaethylporphyrins with Organolithium Reagents

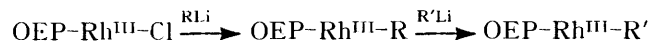
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Nucleophilic attack of organolithium reagents towards the trivalent rhodium-octaethylporphyrin (1) occurs initially at the rhodium atom. Subsequent nucleophilic attack occurs at the meso-position of the porphinate core. Monitoring the reaction by u.v.-visible spectroscopy shows that the axial co-ordination sites are occupied by carbanions to give the hyper-type porphyrin complex (2) at the first stage, and then the phlorin-type complex (3) is formed. Alkyl- and aryl-rhodium(III) complexes (4)–(6) of mono-meso-alkyl- and -aryl-octaethylporphyrins have been obtained by the oxidation of the phlorin-type complexes.

THE substitution reaction at the aromatic meso-position of porphyrins and metalloporphyrins has been investigated in relation to the catabolism of hemoproteins in biological systems.¹ Meso-substituted porphyrins have been obtained by several methods: (i) electrophilic substitution reactions such as Vilsmeier formylations and nitrations;² (ii) electrophilic attack on a porphyrin π -dianion;³ (iii) nucleophilic attack on an oxidized ligand such as a π -dication of porphyrin;⁴ and (iv) isomerization of the ring-expanded porphyrin with diazoesters.⁵ The importance of nucleophilic reactions at the meso-position in the biosyntheses of chlorophylls was established by Woodward.^{4c} In the course of an investigation on a model reaction of coenzyme vitamin B₁₂ by means of rhodium-porphyrin, it was found that two carbanions occupy the axial sites of rhodium-porphyrin to form an anionic complex which changes to an anionic phlorin complex under the reaction conditions used. The latter complex was readily oxidized to the meso-substituted porphyrin complex. This reaction scheme will be discussed in terms of the reaction intermediates detected spectroscopically. The meso-substitution of the rhodium porphyrins was confirmed by ¹H n.m.r. spectroscopy.

RESULTS AND DISCUSSION

The alkyl- and aryl-rhodium(III)-octaethylporphyrins OEP-Rh(III)-R are readily obtained by treatment of chlororhodium(III)-octaethylporphyrin, OEP-Rh(III)-Cl, with alkyl- and aryl-lithium reagents in dry ether. The axial organo-ligand is exchangeable with a second ligand.⁶ When trivalent rhodium complexes are allowed



to react with a large excess of organo-lithium reagent in dry diethyl ether-THF, the colour of the solution turned immediately from orange to brown. The brown solution gradually changed colour to green when stirred overnight under argon at room temperature. Figure 1 shows the change of visible spectrum during the reaction of OEP-Rh^{III}-Me (1) with *p*-methoxyphenyl-lithium. Similar spectral changes were observed using phenyl- and *n*-butyl-lithium.

In general, four routes are possible for the reactions of a carbanion with a metalloporphyrin, *viz.* electron-transfer to the central metal ion or the porphyrin ligand, and bond formation to the metal ion or the porphyrin ligand. Thus the four species (A)–(D) may be responsible for the brown colouration. We assumed the existence of a Rh-C bond in each species to take account of



the fact that the brown solution gave organorhodium(III)-OEP quantitatively when quenched with saturated NH₄Cl solution. The first route to give (A) seems unlikely since treatment of divalent rhodium-porphyrin,⁷ [OEP-Rh^{II}]₂, with organolithium reagents resulted in no Rh-C bond formation. As far as (B) is concerned, although a π -anion radical of a non-transition-metal-porphyrin has been reported,⁸ it is difficult to rationalize the formation of a π -anion radical of a high-valent transition-metal-porphyrin such as (B). The species (D) cannot explain the spectral change because the visible spectrum is not characteristic of either the chlorin or phlorin chromophores, and species reduced or substituted at the peripheral porphyrin ligand could not be detected when the brown solution was quenched as noted above. Co-ordination of a carbanion to the central metal ion is most probable, since the visible spectrum is reasonably interpreted in terms of the six-co-ordinated anionic complex (C) as discussed below. The brown complex (2) has absorption maxima at 375 and 482 nm. This anomalous spectrum, *i.e.* splitting of the Soret band, is typical of the 'hyper' class of porphyrins, and is defined as a 'shifted metalloporphyrin spectrum with the α , β , Soret, and one or more extra bands being present'.⁹ Much interest has been focused on this type of spectrum because a similar splitting was found for the carbon monoxide adduct of cytochrome P-450. The splitting of the Soret band in the u.v.-visible region is explained in terms of mixing of the $\pi \rightarrow \pi^*$ transition of porphyrin ligand with charge-transfer (CT) transition from metal to ligand (*p*-type) or from ligand to metal (*d*-type). A recent theoretical

treatment of the model system of the cytochrome P-450 by an IEH-MO calculation indicated that the filled $p_{z,y}$ orbital on the mercaptide sulphur has the correct symmetry for an allowed $p_{z,y} \rightarrow \pi^*$ CT transition.¹⁰ The sulphur lone-pair p -orbital, $p_{z,y}$, in complex (7) is

In the present reaction conditions strong bases such as carbanions probably co-ordinate at the two axial sites of the trivalent rhodium atom to form an anionic hexacoordinated complex (2). Low-spin d^6 rhodium(III) cannot be a d -type hyperporphyrin because the $e_g(d_{\pi})$ orbitals

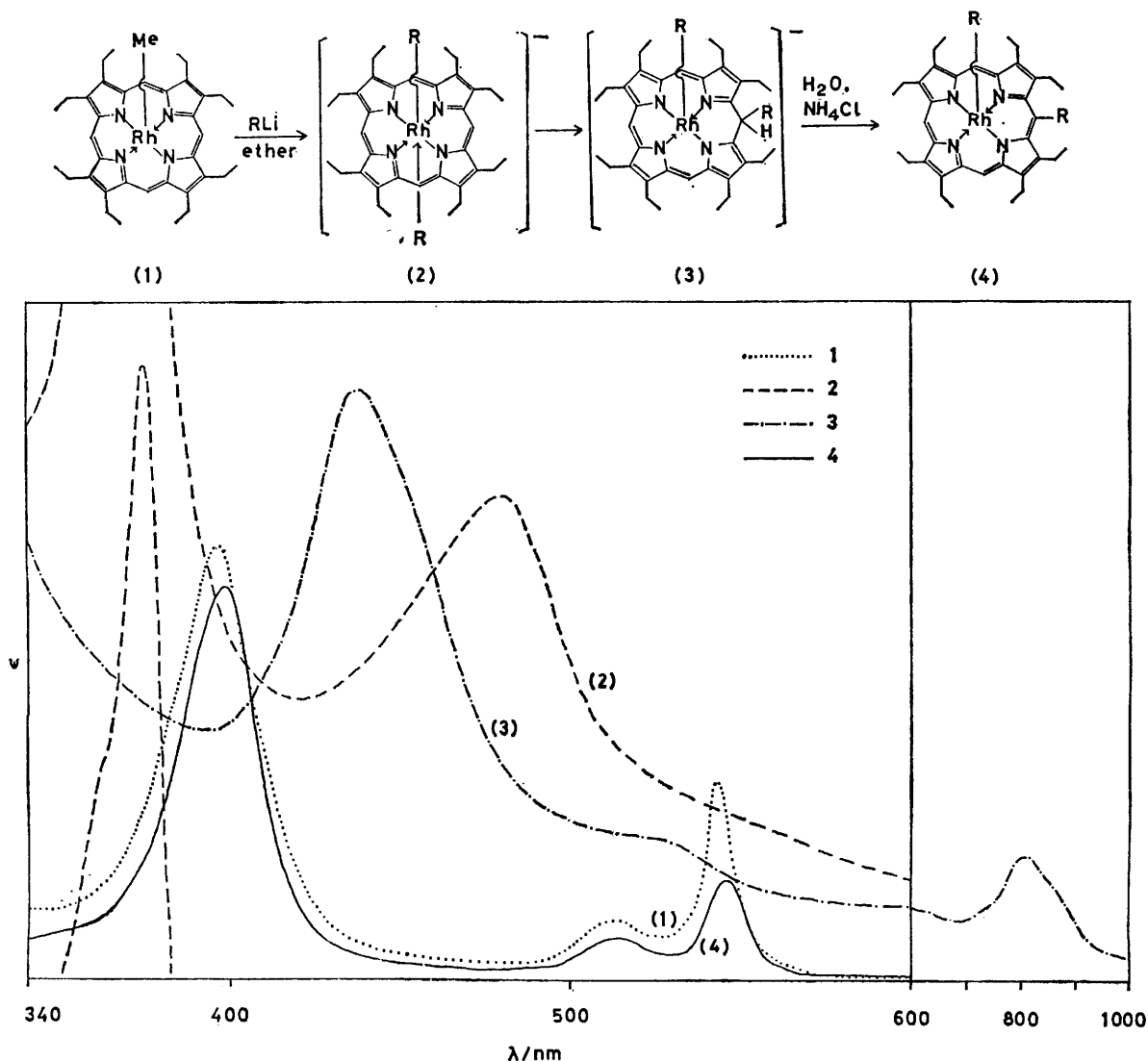
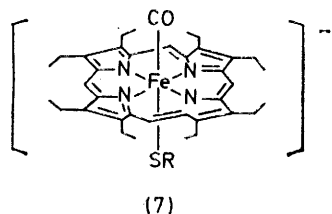


FIGURE 1 The u.v.-visible spectra of compounds (1) and (4), showing also the spectra of the proposed intermediates (2) and (3)

suggested to play the same role as the highest occupied np_z orbital of group 4a and 5a hyper-metalloporphyrins,



such as arsenic(III)-, antimony(III)-, and bismuth(III)-porphyrins. These metalloporphyrins show the strong CT transition to a $\pi^*(e_g)$ orbital of the porphyrin ligand.¹¹

are filled. However, the $5p_z$ orbital is available to bond with two axially co-ordinating carbanions as shown in the qualitative molecular-orbital diagram for complex (2) (Figure 2). The a_{2u} bonding orbital for the axial ligands and metal is constructed from $5p_z(\text{Rh})$, and the two sp^3 (carbon) orbitals of the two axial ligands. This metal-carbon localized orbital is ascribable to the p -type hyper-spectrum of (2), if the transition energy to the $\pi^*(e_g)$ orbital of porphyrin is comparable to that of transitions within the porphyrin ligand.

When OEP-Rh^{III}-Me (1) was allowed to react with an excess of *o*-methoxyphenyl-lithium, formation of the brown compound, which exhibited λ_{max} at 375 and 462

nm, was observed, as shown in Figure 3. However, further spectral changes did not take place under the standard reaction conditions, and the starting material was recovered quantitatively when aqueous NH_4Cl solution was added to the brown solution under argon. This suggests that a mixed-ligand complex occurs, methyl and *o*-methoxyphenyl groups co-ordinating to the fifth and sixth co-ordination sites respectively. The

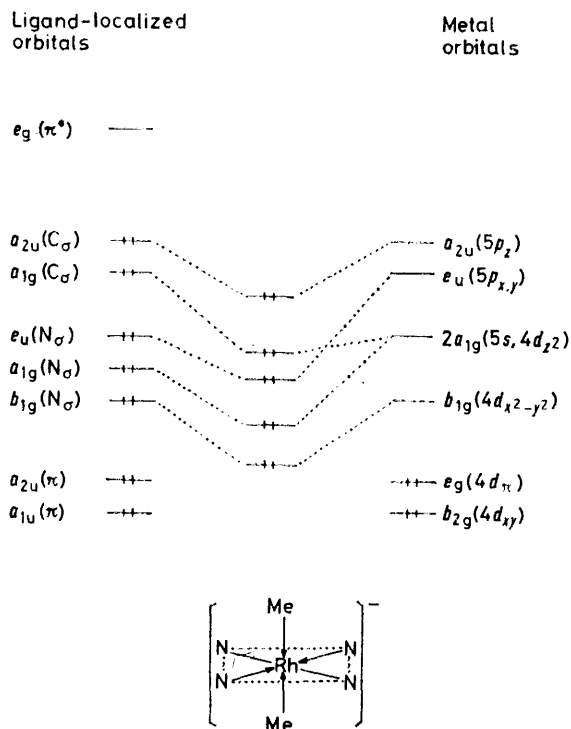


FIGURE 2 Qualitative MO diagram for complex (2)

blue shift of the absorption in the visible region from 482 nm to 462 nm indicates that the structure and bonding of the mixed-ligand complex differ slightly from those of (2). The inability of *o*-methoxyphenyl-lithium to cause meso-substitution is probably ascribed to its weak basicity rather than any steric constraints, since the reaction of (1) with *o*-tolyl-lithium gave the meso-substituted complex.*

The green compound (3) shows λ_{max} at 438 and 805 nm. The band at longer wavelength is characteristic of phlorin compounds.⁸ Phlorins have one saturated methylene bridge where the cyclic conjugation of the aromatic π -system is blocked. These unstable species have been generated from highly reactive ionic substrates such as the π -dication or π -dianion of Zn(II) -porphyrins.⁸ The rhodium-phlorin complex (3) could not be isolated in a stable form due to its extreme sensitivity to air.

* This complex, *o*-tolylrhodium(III)-mono-meso-*o*-tolyl-octaethylporphyrin (34% yield) was found to be composed of two isomers which have not yet been separated. The ^1H n.m.r. spectrum of the product mixture shows two singlets due to the methyl protons of the axial *o*-tolyl ligand at δ -2.13 and -2.24 (ca. 1:1 ratio). The two isomers are considered to result from the inhibition of rotation of the meso-aryl substituent, which is hindered by the adjacent two ethyl groups.

Formation of the phlorin complex was supported by the ^1H n.m.r. spectrum of the green solution prepared from (2) and *n*-butyl-lithium. Although signals due to solvent and *n*-butyl-lithium obscured the δ 0–6 region and prevented us from assigning the signals due to rhodium-porphyrin, we have confirmed that no signal is present either in the aromatic region or to high field of SiMe_4 . This indicates the absence of a diamagnetic ring current of the porphyrin ring. The rhodium-phlorin complex is considered to be derived either *via* nucleophilic attack of the carbanion on the meso-position of complex (2) or intramolecular migration of the axially co-ordinated carbanion to the meso-position. The latter scheme seems to be preferable because nucleophilic attack of a carbanion on the anionic species (2) is unlikely to occur. Formation of the phlorin complex is facilitated by a strongly electronegative metal in a high oxidation state. However, concerted electron transfer from the carbanion to the metal ion may take place as an alternative scheme.

The addition of saturated aqueous NH_4Cl solution to the green solution under argon led to the formation of organorhodium(III) complexes of the mono-meso-substituted octaethylporphyrins (4)–(6), which have been isolated by column chromatography and recrystallization. The ^1H n.m.r. spectra of these complexes show two singlets for the meso-proton in the ratio of 2:1. The signals of the eight ethyl groups are split owing to the lowering of the molecular symmetry. In particular, the two ethyl groups adjacent to the meso-aryl substituent resonate at ca. 1.0 p.p.m. to higher field of the other six ethyl groups, due to the diamagnetic ring-current effect of the meso-aryl group (Figure 4). Moreover, the meso-substitution by the aryl group was verified by comparing the ^1H n.m.r. spectra with that of the mono-meso-aryloctaethylporphyrin prepared *via* an alternative pathway.¹²

This work has offered the first example of the reaction of a nucleophile with a neutral metalloporphyrin at the meso-position of the porphinato-ligand. A higher-valent central metal atom in metalloporphyrins would decrease electron density on the meso-positions, and this would enhance the reactivity of the meso-positions towards nucleophilic reagents.

EXPERIMENTAL

Spectral Measurements.—Infrared, ^1H n.m.r., and u.v.-visible spectra were recorded on a Hitachi EP1-G31 grating spectrophotometer, a Varian HA-100 spectrometer, and a Hitachi EPS-3T recording spectrophotometer, respectively. The u.v.-visible spectra of (2) and (3) were recorded under argon, using a cell of thickness 0.1 mm.

General Procedure.—The organolithium reagent (1.0–1.5 mmol) was added dropwise to a dry THF (20 ml) solution of OEP-Rh(III)-Me (1) (65 mg, 0.1 mmol). On the addition of ca. 0.5 ml (0.5–0.75 mmol) of organolithium solution, the colour of the solution changed from orange to brown. Then a further ca. 0.5 ml of organolithium reagent was added and the brown solution was stirred for 5 h at room temperature under argon, which resulted in the formation of a green solution. When saturated aqueous NH_4Cl

solution (5 ml) was added to this solution, the colour of the solution changed immediately from green to orange. The aqueous layer was separated and discarded, and the organic layer was washed with water and dried over Na_2SO_4 .

Compound (4; R = *p*-methoxyphenyl): δ (CDCl_3) 10.07 (s, $2 \times -\text{CH}=\text{}$), 10.05 (s, 1 H, $-\text{CH}=\text{}$), 8.17 (m, 1 H, meso-*p*-methoxyphenyl *ortho*-H), 7.90 (m, 1 H, meso-*p*-methoxyphenyl *ortho*-H), 7.18 (m, 2 H, meso-*p*-methoxyphenyl

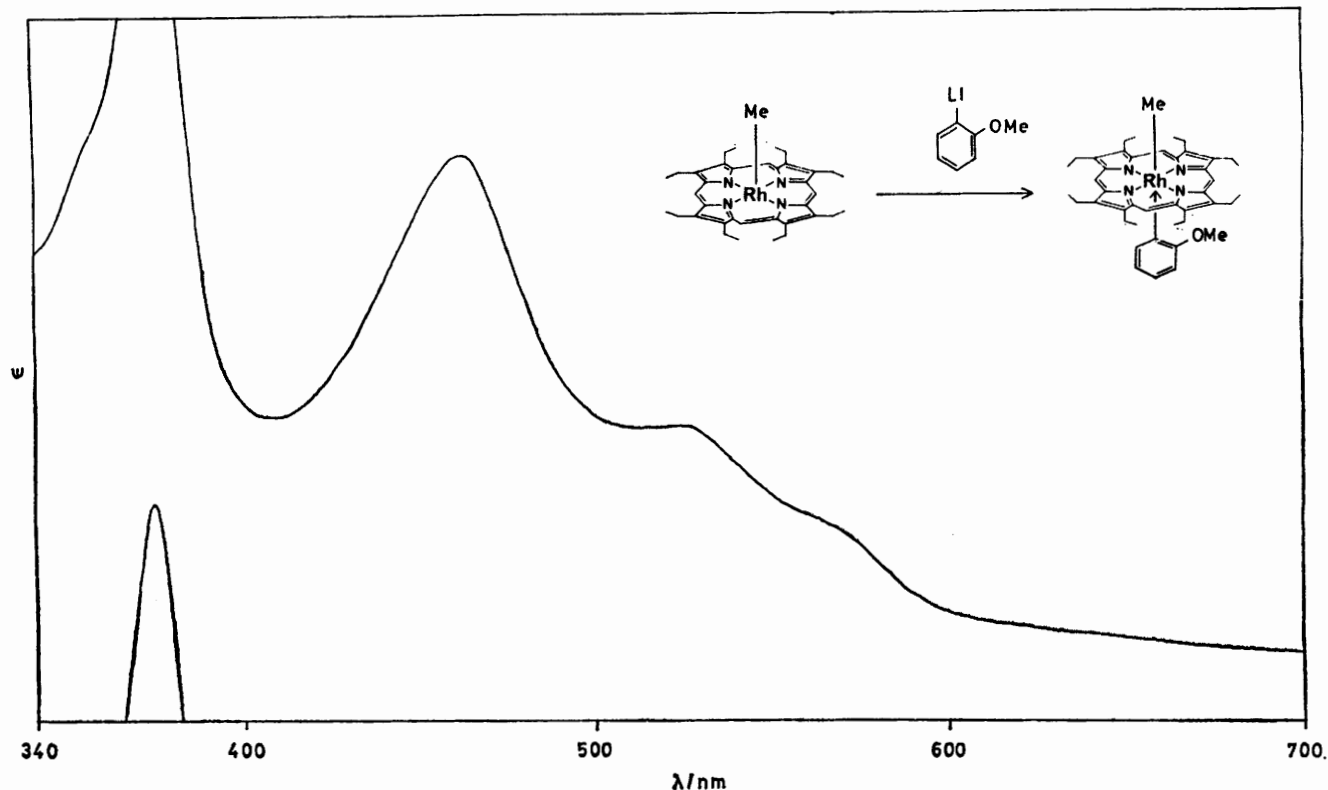


FIGURE 3 Visible spectrum of a solution of compound (1) and *o*-methoxyphenyl-lithium

Chromatography (silica gel column) eluted first a red band [benzene-*n*-hexane (1:1)], which afforded red crystals by recrystallization from CH_2Cl_2 - CH_3OH . The complexes, meso-R-OEP-Rh^{III}-R [R = *p*-methoxyphenyl (4), phenyl (5), or *n*-butyl (6)], were obtained in 68, 77, and 23% yield, respectively.

meta-H), 4.26 (d, 2 H, Rh-*p*-methoxyphenyl *meta*-H), 4.07 (s, 3 H, meso-*p*-methoxyphenyl OMe), 3.98 (m, 12 H, $6 \times \text{CH}_2\text{Me}$), 2.74 (m, 4 H, $2 \times \text{CH}_2\text{Me}$), 2.67 (s, 3 H, Rh-*p*-methoxyphenyl OMe), 1.91, 1.89, and 1.84 (all t, 18 H, $6 \times \text{CH}_2\text{Me}$), 1.15 (t, 6 H, $2 \times \text{CH}_2\text{Me}$), and -0.23 (dd, 2 H, Rh-*p*-methoxyphenyl *ortho*-H); λ_{max} (CHCl_3) 399

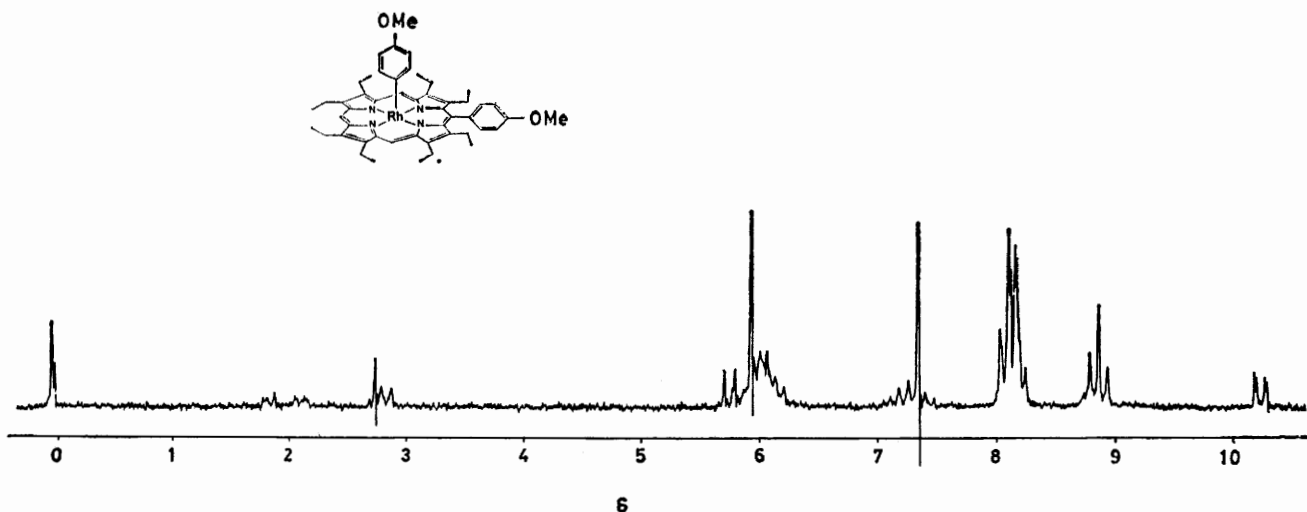


FIGURE 4 ^1H N.m.r. spectrum of mono-meso-*p*-methoxyphenyl-OEP-Rh^{III}-*p*-methoxyphenyl (4)

(log ϵ 5.29), 513 (4.23), and 546 nm (4.65) (Found: C, 70.75; H, 6.95; N, 6.65. Calc. for $C_{90}H_{89}N_4O_2Rh$: C, 70.74; H, 6.77; N, 6.60%).

Compound (5; R = phenyl): δ ($CDCl_3$) 10.06 (s, 2 H, $2 \times -CH=$), 10.05 (s, 2 H, $2 \times -CH=$), 8.29 (m, 1 H, meso-phenyl *ortho*-H), 8.02 (m, 1 H, meso-phenyl *ortho*-H), 7.66 (m, 3 H, meso-phenyl *meta*- and *para*-H), 5.11 (t, 1 H, Rh-phenyl *para*-H), 4.59 (t, 2 H, Rh-phenyl *meta*-H), 3.98 (m, 12 H, $6 \times CH_2Me$), 2.61 (m, 4 H, $2 \times CH_2Me$), 1.89, 1.87, 1.82 (all t, 18 H, $6 \times CH_2Me$), 1.12 (t, 6 H, $2 \times CH_2Me$), and -0.13 (d, 2 H, Rh-phenyl *ortho*-H); λ_{max} . ($CHCl_3$) 399 (log ϵ 5.00), 513 (4.06), and 546 nm (4.57) (Found: C, 72.7; H, 6.95; N, 7.0. Calc. for $C_{48}H_{53}N_4Rh$: C, 73.07; H, 6.77; N, 7.10%). Compound (6; R = n-butyl): δ ($CDCl_3$) 9.79 (s, 2 H, $2 \times -CH=$), 9.75 (s, 1 H, $-CH=$), 4.90 (t, 2 H, meso- CH_2), 3.94 (m, 16 H, $8 \times CH_2Me$), 1.86, 1.83, and 1.74 (all t, 24 H, $8 \times CH_2Me$), 1.24 (m, 4 H, meso- $CH_2-[CH_2]_2Me$), 0.70 (m, 3 H, meso- $[CH_2]_3Me$), -0.99 (t, 3 H, Rh- $[CH_2]_3Me$), -1.75 (m, 2 H, Rh- $[CH_2]_2CH_2Me$), -4.75 (m, 2 H, Rh- $CH_2CH_2CH_2Me$), and -5.23 (m, 2 H, Rh- $CH_2[CH_2]_2Me$); λ_{max} . ($CHCl_3$) 404 (log ϵ 5.04), 519 (4.07), and 547 nm (4.25) (Found: C, 70.35; H, 8.3; N, 7.55. Calc. for $C_{44}H_{61}N_4Rh$: C, 70.56; H, 8.21; N, 7.48%).

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